Alkylation and addition to isocyanate of 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide. X-Ray crystal and molecular structures of methyl-, dimethyl-, dimethylaminoethylene- and propylaminocarbonyl-amino derivatives

Vincenzo Fares,*[a] Alberto Flamini *[b] and Pamela Pasetto[b]

[a] *Istituto di Strutturistica Chimica, Area della Ricerca di Roma/Montelibretti,
  00016 Monterotondo Stazione (Roma), Italy*
[b] *Istituto di Chimica dei Materiali del CNR, Area della Ricerca di Roma/Montelibretti,
00016 Monterotondo Stazione (Roma), Italy*

Several substituents have been introduced on the amino group of 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (C_5N_3–$C_4N(CN)_2$–NH_2^-, L′) to give the derivatives C_5N_3–$C_4N(CN)_2$–$NHCH_3^-$ (**1**), C_5N_3–$C_4N(CN)_2$–$N(CH_3)_2^-$ (**2**), C_5N_3–$C_4N(CN)_2$–$NHCH_2C_6H_5^-$ (**3**), C_5N_3–$C_4N(CN)_2$–$N=CHN(CH_3)_2^-$ (**4**) and C_5N_3–$C_4N(CN)_2$–$NHCONHCH_2CH_2CH_3^-$ (**5**) that have been characterized by elemental analysis and IR, UV–Vis and ^{1}H-NMR spectroscopy. The reactions carried out were nucleophilic substitution for **1** and **2**, condensation with aromatic aldehydes and subsequent reduction for **3**, condensation with amido-acetals for **4** and addition to isocyanates for **5**. The main optical band of these compounds is shifted to lower or higher energy in comparison to L′. These shifts are easily accounted for by the inductive or mesomeric substituent effect on the amino group of L′. The X-ray crystal and molecular structures of **1**, **2**, **4** and **5** have been determined from diffraction studies on single crystals of their tetraphenylarsonium salts. The geometrical features of the four anions, together with those of the previously reported L′ and salicylideneamino derivative C_5N_3–$C_4N(CN)_2$–$N=CHC_6H_4OH^-$, allow us to see the effects of the substituents and of the crystal packing interactions on the electronic charge distribution within the tricyanovinyl-2*H*-pyrrole conjugated system. While **1** and **3** behave as chelating ligands towards transition metal cations, as does L′, the other anions do not. The absence of hydrogen atoms on the amino group (in the case of **2** and **4**) and the steric hindrance due to strong intramolecular hydrogen bonds (in the case of **5**) prevent chelation.

Introduction

The title anion, C_5N_3–$C_4N(CN)_2$–NH_2^- (L′, Scheme 1), which we synthesized for the first time from tetracyanoethylene (TCNE),[1] is the precursor of several bis(diiminotetracyano-pyrrolizinato)metal(II) complexes ML_2,[2–6] which are of considerable interest both in material science and in theoretical calculations.[7–8] With the aim of exploiting L′ or its derivatives in practical applications, as in the construction of optochemical sensors, we have been studying their photometric properties, potentially useful for detecting species of environmental interest. We found that the following systems could be used as chemical sensors: (i) NaL′, embedded in sol–gel matrices, for Hg^{2+} in water,[9] (ii) evaporated LH thin film, for gaseous ammonia[10] and (iii) NiL_2, incorporated in a preformed, unplasticized polymer, for organic solvent vapors.[11] But such sensor systems have several drawbacks, which would limit their practical use: in (i) the entrapment of L′ is not reliable in terms of stability as a consequence of the continuous leakage of L′ itself by water, in (ii) and (iii) the sensitivity within a reasonable response time is low due to the limited accessibility of the indicator to the analyte. Now, in order to improve their performance, we sought to modify L′ by chemical substitution, such that the resulting products could be deposited on the surface of the various supports as covalently bound molecular monolayers or Langmuir–Blodgett films. The replacement of one hydrogen atom of the amino group of L′ by a proper substituent is the only accessible route to this end. In fact, the apparently easier alternative, involving the use of a tricyano-ethylene derivative as the starting material instead of TCNE for producing a corresponding L′ analogue, is not possible, since

tricyanoethylenes, under the reaction conditions adopted for the formation of L′ from TCNE, furnish the tetracyanotetra-azaporphyrins.[12] Several strategies based on the chemistry of the amino group have been applied. Here we report the alkylation, in one- and two-step procedures, and the addition of isocyanate. The X-ray crystal and molecular structures of the methyl-, dimethyl-, dimethylaminomethylene- and propyl-aminocarbonyl-amino-L′ derivatives as tetraphenylarsonium salts are also reported.

Results and discussion

Chemical substitution

Starting from the work by H. R. Sommer and co-workers on the exhaustive alkylation of primary amines,[13] we readily found the best conditions for obtaining the desired product. The reaction with an aliphatic iodide taken in excess, in a polar solvent, in the presence of a strong, but poorly nucleophilic base, under moderate heating was enough to achieve this. The bis-substituted derivative is also concomitantly formed, in a variable proportion relative to the mono-substituted compound, depending on the excess amount of the alkylating agent and on the temperature and extent of the reaction. Fortunately, the two products can be separated and purified by column chromatography as their tetraphenylarsonium salts. In particular, by reaction with a fivefold excess of CH_3I in DMF in the presence of *N,N,N′,N′*-tetramethylnaphthalene-1,8-diamine, at 90 °C, during 45 min, L′ is converted into 26% of mono-substituted **1** and 3% of bis-substituted **2**. The yield of **2** is increased up to 22% by doubling the excess amount of
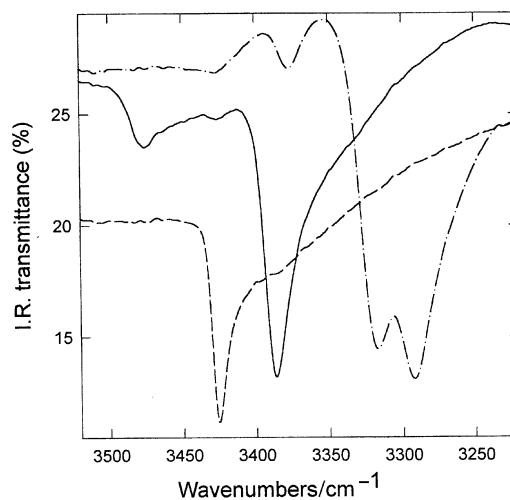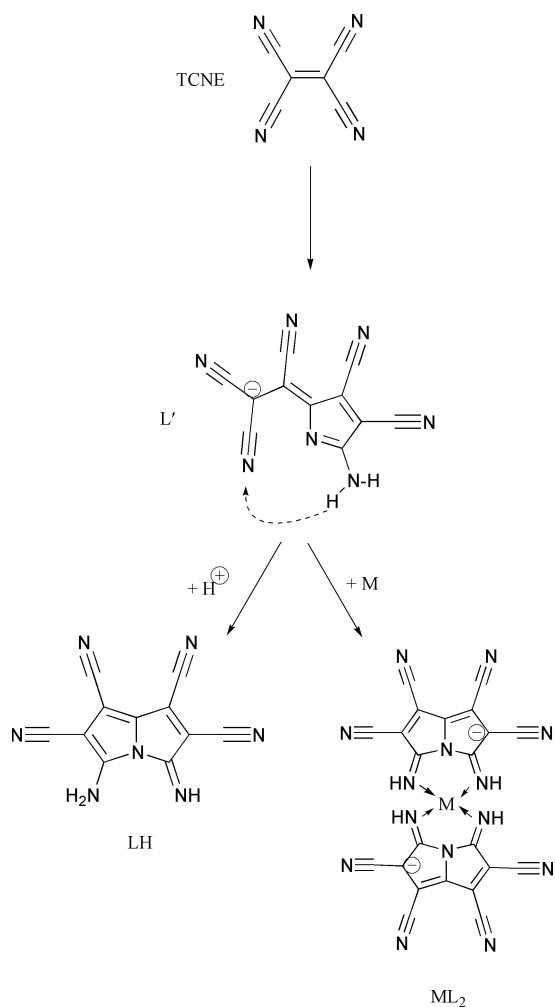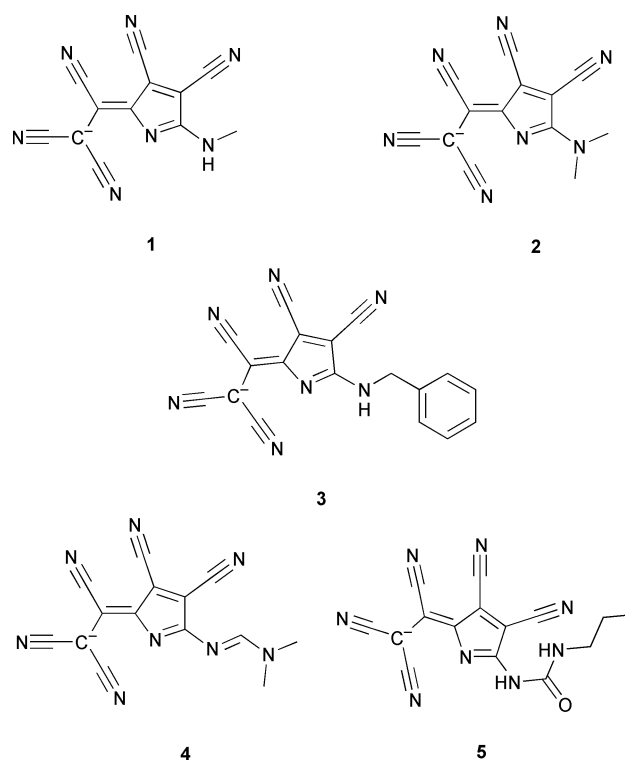
DOI: 10.1039/b003407j

Scheme 1

CH₃I and the reaction time (see Experimental). The ^{1}H-NMR spectra clearly support the given formulae and are directly related to the spectrum of the starting material in the same solvent, AsPh₄L′ in CDCl₃: 7.57–8.00 ppm (20 phenyl-H), 4.61 ppm (2 NH).[14] The IR spectra are similarly informative, at least in the region where the N–H stretching vibrations fall (3600–3200 cm⁻¹, Fig. 1). Moreover, a notable difference between L′ and **1** appears, with the stretching frequency in the latter species being shifted to higher energy relative to the former. As reported in the literature,[15] this is characteristic of hydrogen bonds involving the N–H group and, in this instance, it implies that the hydrogen bond in question is weaker in **1** than in L′. Accordingly, the results from the X-ray analysis (see below) are consistent with this expectation.

As far as the two-step alkylation procedure is concerned (condensation with aldehydes and reduction), our previous studies on the condensation of L′ with aldehydes [16] show that only aromatic aldehydes react to produce the corresponding alkylideneamines. We now focus on the second step in the current work. We found that the benzylideneamine anion C₅N₃–C₄N(CN)₂–N=CHC₆H₅⁻ is reduced regiospecifically by NaBH₃CN–AcOH in EtOH to the corresponding benzyl derivative, C₅N₃–C₄N(CN)₂–NHCH₂C₆H₅⁻ **3**. As expected, the spectral features of **3** parallel those of **1** (see Experimental), and moreover, the metal complexation properties of the two anions are comparable (see below). In this context, we examined also the reactivity of aldehydo- and amido-acetals in the condensation with L′. The aldehydo-acetals do not react while the amido-acetals do react under mild conditions in a quantitative yield. The resulting amidino-amino-L′ derivative is stable in water and is not reduced by NaBH₃CN. In particular, the dimethyl-aminomethyleneamino derivative **4** has been characterized by single crystal X-ray analysis, as reported below.

Anion L′ adds to aliphatic isocyanates readily in the presence of triethylamine as a catalyst. The resulting aminocarbonyl derivative shows the expected spectral features. In particular, the propylaminocarbonyl **5** exhibits two distinct infrared N–H stretching bands, both at lower energy with respect to the same band in L′ (Fig. 1). Again, as for **1**, this difference can be accounted for by the X-ray crystal structure data. In fact, as reported and explained in the next section, the hydrogen bonds involving the N–H groups are both stronger in **5** than in L′.

Regarding the optical spectra, we observe that for the series L′→**1**→**2**, the main absorption band is shifted to lower energy (Fig. 2 and Table 1). A simple explanation of this trend may be found by considering that these compounds belong to the class of hemicyanine dyes[17] and therefore their main absorption band, due to the ππ* HOMO→LUMO transition, involves some intramolecular charge transfer from the donor to the acceptor groups. Specifically in this case, the amino and the cyano groups are the donor and acceptor, respectively, and thus

Table 1 Significant geometrical and spectral features of the seven anions containing the tricyanovinyl-2*H*-pyrrole system, grouped according to the amino-substituent type

Compound	Ref.	Type[a]	N8–C2[b]	C2–N1[b]	N1–C5[b]	C5–C6[b]	C6–C7[b]	λ_{max}(CH$_2$Cl$_2$)/nm[c]
2		–NRR	1.35	1.32	1.36	1.39	1.39	606
1		–NRH	1.35	1.34	1.39	1.40	1.40	576
L'$_a$	14	–NHH	1.35	1.34	1.39	1.40	1.40	550
5		–NR^{1}H*	1.38	1.33	1.37	1.41	1.38	532
L'$_b$	14	–NHH*	1.37	1.33	1.38	1.41	1.38	550
4		–NR^2	1.39	1.35	1.36	1.42	1.38	579
L'–salycil	16	–NR^3	1.41	1.33	1.36	1.42	1.37	522

[a] Substituents on the amino group: R –CH$_3$, R^1 –CONHCH$_2$CH$_2$CH$_3$, R^2 =CHN(CH$_3$)$_2$, R^3 =CHC$_6$H$_4$OH; (H* = hydrogen involved in strong inter/intramolecular interactions). [b] Bond lengths in Å, with esds ≤ 0.01 Å. [c] Maxima of the main absorption optical bands.
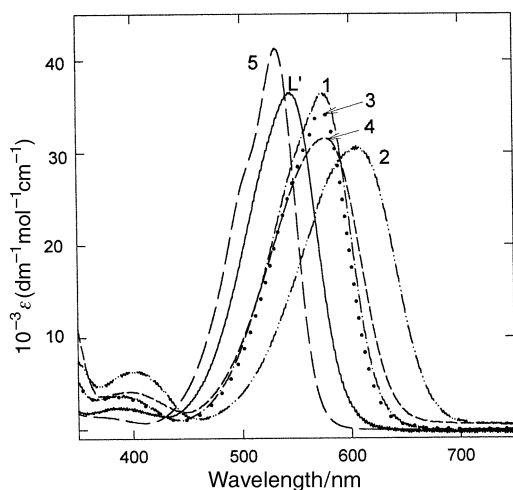

Fig. 2 Normalized solution optical spectra in CH$_2$Cl$_2$ of the tetraphenylarsonium salt of (——) L', (–·–) **1**, (–··–) **2**, (······) **3**, (- - - - -) **4** and (– – –) **5**.

their π orbitals contribute differently to the L' frontier orbitals: those from –NH$_2$ being predominant in the HOMO and those from –CN groups in the LUMO. Finally, the replacement of H by CH$_3$ in –NH$_2$ raises the HOMO energy because of the +Is effect (positive inductive effect) of the CH$_3$ substituent, resulting in an overall reduction of the HOMO→LUMO transition energy (HLTE). Similarly, we observe that +Is and +M effect (positive mesomeric effect) effect is operative in the benzyl and the dimethylaminomethyleneamino derivatives, respectively, while the −Is effect (negative inductive effect) operates in both the propylaminocarbonylamino and previously reported [16] salicylideneamino derivative C$_5$N$_3$–C$_4$N(CN)$_2$–N=CHC$_6$H$_4$OH$^-$, with an increase in HLTE and a band-shift to higher energy.

X-Ray crystal structures of the tetraphenylarsonium salts of the L' amino-substituted anions C$_5$N$_3$–C$_4$N(CN)$_2$–NHCH$_3^-$ 1, C$_5$N$_3$–C$_4$N(CN)$_2$–N(CH$_3$)$_2^-$ 2, C$_5$N$_3$–C$_4$N(CN)$_2$–N=CHN-(CH$_3$)$_2^-$ 4, and C$_5$N$_3$–C$_4$N(CN)$_2$–NHCONHCH$_2$CH$_2$CH$_3^-$ 5

The molecular structures and the main interatomic distances and angles of the four title L' derivatives are shown in the Figs. 3–6 respectively. The anion **1** is not quite as planar as expected, but slightly distorted, with the N(14) and C(81) atoms showing an out-of-plane displacement of 0.80 and −0.34 Å respectively, due to a weak attractive N(14)···H(8)′ interaction of 2.98 Å and a repulsive one H(CH$_3$)···H′(CH$_3$) of 2.01 Å between the two centrosymmetrical units. Its structural details can be compared with those of the unsubstituted L' (two polymorphic, orthorhombic (**a**) and monoclinic (**b**) forms),[14] characterized by stronger –CN···HN– intermolecular hydrogen bonds, ranging between 2.31 Å in L'$_a$ and 2.52 Å in L'$_b$.
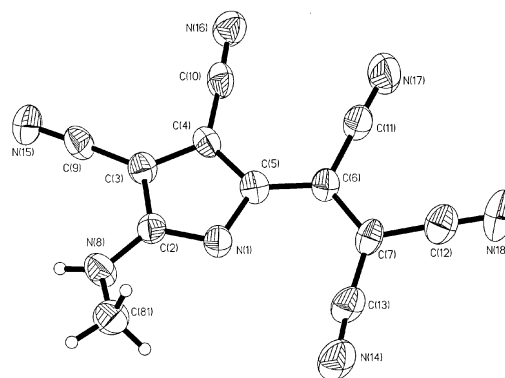
Fig. 3 Molecular structure of anion **1**. Thermal ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(2) 1.34(1), N(1)–C(5) 1.39(1), C(2)–C(3) 1.42(1), C(2)–N(8) 1.35(1), C(3)–C(4) 1.37(1), C(4)–C(5) 1.43(1), C(5)–C(6) 1.39(1), C(6)–C(7) 1.39(1), N(8)–C(81) 1.45(1); C(2)–N(8)–C(81) 121.2(9).
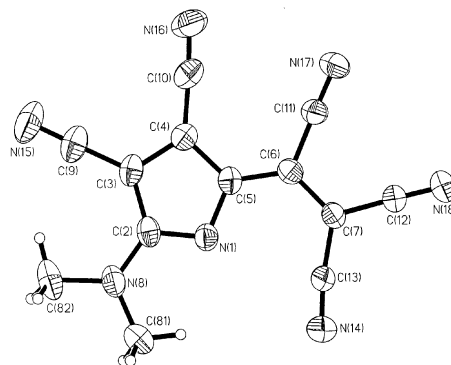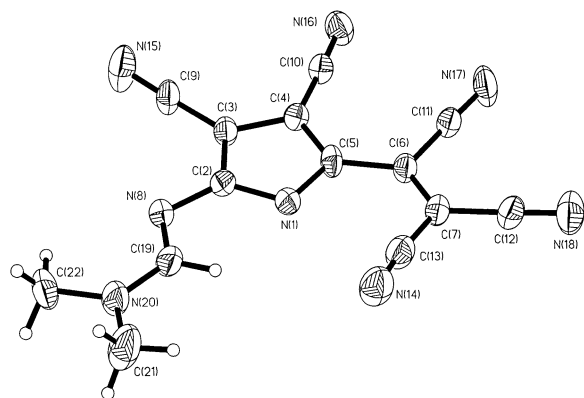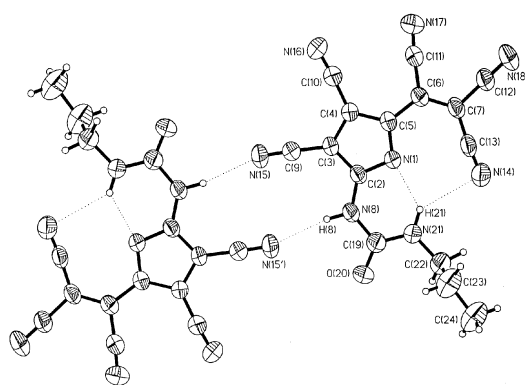

Fig. 4 Molecular structure of anion **2**. Thermal ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(2) 1.321(6), N(1)–C(5) 1.363(6), C(2)–C(3) 1.424(7), C(2)–N(8) 1.349(7), C(3)–C(4) 1.413(7), C(4)–C(5) 1.434(7), C(5)–C(6) 1.385(6), C(6)–C(7) 1.391(6), N(8)–C(81) 1.416(7), N(8)–C(82) 1.435(7); C(2)–N(8)–C(81) 120.5(4), C(2)–N(8)–C(82) 123.8(5).

Anion **2**, which consists of discrete molecular units without significant interactions, is almost planar, with the two methyl carbon atoms at 0.11 and −0.15 Å from the rms plane.

The discrete anion units of **4** are also essentially planar, the maximum out-of-plane displacement being 0.27 Å for two terminal N(14) and N(15) nitrogen atoms. The dimethylaminomethylamine bond distances can be compared with the analogous ones reported for its tris(trifluoromethyl)borane complex,[18] where the electronic charge is delocalized over the two C–N bonds with two equivalent distances of 1.30 Å. In our case, two significantly different values of 1.33 and 1.29 Å are found for the homologous C(19)–N(20) and N(8)–C(19) bond lengths respectively, which, together with the value of 1.39 Å found for the N(8)–C(2) distance, indicate a high degree of charge localization over the N(8)–C(2) bond. This situation is

Fig. 5 Molecular structure of anion **4**. Thermal ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(2) 1.35(1), N(1)–C(5) 1.36(1), C(2)–C(3) 1.40(1), C(2)–N(8) 1.39(1), C(3)–C(4) 1.41(1), C(4)–C(5) 1.40(1), C(5)–C(6) 1.42(1), C(6)–C(7) 1.38(1), N(8)–C(19) 1.29(1), C(19)–N(20) 1.33(1), N(20)–C(21) 1.42(2), N(20)–C(22) 1.43(1); C(2)–N(8)–C(19) 116.0(7), N(8)–C(19)–N(20) 123.5(8), C(19)–N(20)–C(21) 121.7(8), C(19)–N(20)–C(22) 121.4(9).


Fig. 6 Two of the centrosymmetric molecular units of anion **5**. Inter- and intra-molecular hydrogen bonds are shown by dotted lines. Thermal ellipsoids are at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(2) 1.326(5), N(1)–C(5) 1.368(5), C(2)–C(3) 1.413(4), C(2)–N(8) 1.383(5), C(3)–C(4) 1.396(5), C(4)–C(5) 1.416(5), C(5)–C(6) 1.414(5), C(6)–C(7) 1.383(5), N(8)–C(19) 1.392(5), C(19)–O(20) 1.229(5), C(19)–N(21) 1.332(5), N(21)–C(22) 1.462(6), C(22)–C(23) 1.50(1), C(23)–C(24) 1.524(8); C(2)–N(8)–C(19) 128.7(3), N(8)–C(19)–N(21) 117.2(4), C(19)–N(21)–C(22) 120.4(4).

very similar to that present in the L′-salicylideneamino derivative,[16] where a C=N amido double bond of 1.27 Å is present.

Anion **5**, in contrast to the derivatives described above, consists of pairs of co-planar centrosymmetric units which, through H(8)···N(15′) intermolecular H-bonds of 2.30 Å, give rise to dimeric moieties (see Fig. 6). Moreover, strong intramolecular H···N interactions H(21)···N(1) and H(21)···N(14), of 2.01 and 2.53 Å, respectively, are found. The two –NH groups, involved in H-bonds of different strength, account for the IR spectra discussed above, and, on the basis of the structural results, allow easy assignment.

The four anions described here, together with L′ₐ, L′_b, and salicylideneamine, make an homogeneous series of related, structurally characterized, compounds, which provide more detailed information about the influence of different amino substituent groups on the electronic charge distribution within the tricyanovinyl-2*H*-pyrrole conjugated system. By considering the seven anions (see Table 1), a significant variation of the C(2)–N(8) bond length is evident in connection with both the chemical nature of the substituents and the crystal packing interactions. In fact, these distances range from 1.35 Å in **2**, **1** and L′ₐ, where only slight solid-state interactions are present, to 1.37–1.38 Å in **5** and L′_b, where the L′ amino group is involved in significant hydrogen bonds. The –C=N– amido double bond in both the dimethylaminomethyleneamino (**4**) and salicyl-
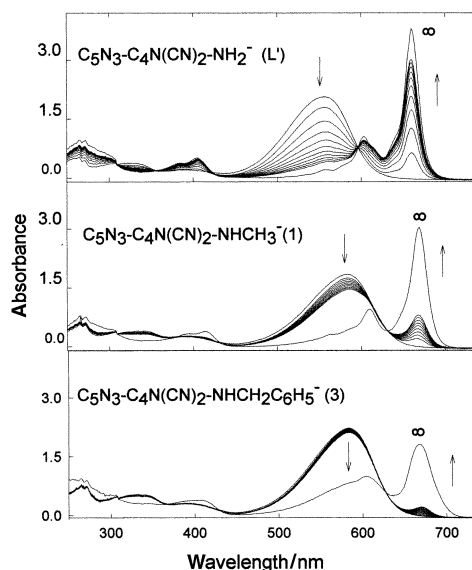
Fig. 7 Spectral changes with time (every 5 min) of ethanol solutions (95% ethanol in water) of the tetraphenylarsonium salts of L′, **1** and **3** (2.5 cm³; $c = 7.28 \times 10^{-5}$, 7.18×10^{-5} and 8.67×10^{-5} M, respectively; pathlength = 1 cm) after adding an ethanol solution of NiCl₂·6H₂O ($c = 7.6 \times 10^{-4}$ M) in an amount (≈0.5 cm³) such that the resulting total molar ratio of the reagents (metal : ligand) is 2.0 for each solution. Arrows indicate the direction of the spectral changes. The curves marked with '∞' were recorded after the spectral changes had stopped (18 h).

ideneamino derivatives causes an increase in the C(2)–N(8) distance to 1.39–1.41 Å. Analogously, anions **2**, **1** and L′ₐ display a high degree of charge delocalization (note, in Table 1, the similarity of the bond length values for N(8)–C(2) and C(2)–N(1) on the one hand, and for N(1)–C(5), C(5)–C(6), and C(6)–C(7) on the other), while in the remaining four anions the corresponding bond lengths indicate a net loss of conjugation.

Metal complexation studies

Only anions **1** and **3** react similarly to L′ with late transition metal(II) cations to yield pyrrolizinato complexes. However, the kinetic and thermodynamic parameters of the coordination reaction are somewhat different for the three anions. An appropriate comparison is presented in Fig. 7. It is evident that substitution on the amino group slows down the reaction from L′ to **3**. Looking at the stationary absorbance curves (∞) in the same Figure, it is also evident that the equilibrium constants of the three reactions are qualitatively affected by the substitution in the same way as the kinetic parameters, that is, they decrease along the series L′→**1**→**3**. The differences in the coordination reaction kinetics can be explained easily. One hydrogen atom of the amino group must migrate to the nitrogen atom of the nitrile adjacent to the pyrrole (Scheme 1) in order for the metal complexation to occur. Consequently, the coordination is faster with L′ than with the monosubstituted derivatives, since there are two hydrogen atoms available on the amino group in L′ while there is only one in the derivatives. Furthermore, in **1** the substituent lies on the molecular plane facing the pyrrole ring, because of the attractive interaction between the methyl hydrogen and the pyrrole nitrogen. Presumably, the same occurs in **3** with the benzyl substituent. Thus, for these derivatives the metal coordination also involves prior rotation by 180° of the amino group about the pyrrole–amino C(2)–N(8) bond. Obviously, the hindrance to such rotation is dependent on the nature and dimensions of the substituent. Incidentally, we note that in **5** the same rotation should be severly hindered by the intramolecular hydrogen bonds (Fig. 6), and thus, this molecule does not behave as a chelating ligand in solution at room temperature, although it still has one hydrogen atom available on the amino group.

To test the possibility of covalently binding L′ on the surface of a suitable support (sol–gel silica) for application in sensor devices for heavy metal cations in water, we carried out several experiments based on the current results. In particular, the derivatives C_5N_3–$C_4N(CN)_2$–$NHCH_2CH_2CH_2Si(OCH_3)_3^-$ (L′$_1$) and C_5N_3–$C_4N(CN)_2$–$NHCONHCH_2CH_2CH_2Si(OCH_3)_3^-$ (L′$_2$) have been prepared, although it was not possible to purify them adequately. They bind to silica surfaces under mild conditions, as expected for trialkoxysilyl derivatives.[19] The resulting L′-doped silica composites (L′/SiO$_2$) have been evaluated as sensors for Hg^{2+}. The L′$_1$/SiO$_2$ composite showed fairly good sensor parameters,[20] correlated with those of **1** in homogeneous solution. L′$_2$/SiO$_2$, which is still under study,[21] shows a reactivity towards Hg^{2+} comparable to that of L′$_1$/SiO$_2$ and thus, completely different from that of **5** in homogeneous solution, where it does not chelate any metal cations. Perhaps, the intramolecular hydrogen bonds are no longer present in L′$_2$ on silica but rather, all possible hydrogen bonds are formed with the oxygen atoms of the matrix without hindering metal complexation.

Conclusions

Several well-known reactions of primary amines have been successfully carried out on L′ affording the corresponding amino-substituted L′ derivatives. By using the appropriate reagents, the homologous derivatives have been prepared, which also contain the –Si(OR)$_3$ group and are suitable for covalent binding on silica surfaces. The L′ derivatives behave as chelating ligands towards transition metal cations in solution in the same way as L′, by undergoing an intramolecular cyclization through the migration of an hydrogen atom from the L′ amino group to a cyano group. This is therefore possible provided that the amino group bears at least one hydrogen atom, or that the conformational changes required for the chelation are not hindered by strong intramolecular interactions as in the case of **5**. Generally, silica surfaces, being very active hydrogen bond forming supports, effectively change the conformation of the L′ derivatives anchored on it, and so impart to them a reactivity completely different from that shown in homogeneous solution, which is more favorable for application in sensor devices.

Experimental

Melting points were determined on a Büchi SMP-20 model melting point apparatus. Elemental analyses were carried out by Servizio Microanalisi of CNR, Area della Ricerca di Roma. Solution optical spectra were recorded in CH$_2$Cl$_2$ on a Cary 5 spectrometer; the wavelength band maximum (λ/nm), the corresponding extinction coefficient (ε/dm^3 mol^{-1} cm^{-1}) and half-height band width (hhw/nm) are given. IR measurements were performed with a Perkin-Elmer 16F PC FT spectrometer on KBr pellets (0.75% w/w); the stretching frequencies (ν/cm^{-1}) of the absorption maxima of the most significant bands are given. The ^{1}H-NMR spectra were obtained in CDCl$_3$ solution with a Bruker AMX-600 spectrometer. The chemical shifts (δ) were referred to the residual CHCl$_3$ proton (7.238 ppm) of CDCl$_3$. The integrated area of the signals was normalized to the corresponding proton number assuming the aromatic proton signal of tetraphenylarsonium cation (7.50–7.90 ppm, 20 phenyl H) as internal standard. The J-values are given in Hz. All the reactions described below were followed spectrophotometrically taking advantage of the distinctive chromophoric properties of the starting materials and the reaction products.

Materials

Methyl iodide, N,N,N',N'-tetramethylnaphthalene-1,8-diamine or proton sponge (PS), NaBH$_3$CN, acetic acid (AcOH), N,N-

dimethylformamide diethyl acetal, triethylamine, propyl isocyanate (PrNCO) were commercial reagents of Fluka analytical grade. The tetraphenylarsonium salt of L′ (AsPh$_4$·L′)[14] and its condensation product with benzaldehyde (AsPh$_4$·**6**)[16] were prepared following our methods. The reaction solvents, tetrahydrofuran (THF), ethanol (EtOH) and N,N-dimethylformamide (DMF), were carefully dried and freshly distilled before use. In particular, THF and EtOH were refluxed and then distilled at atmospheric pressure under dinitrogen over sodium–benzophenone ketyl and CaO, respectively, while DMF first was dried by azeotropic distillation with benzene and by shaking the remaining liquid with Linde type 4 Å molecular sieves and then was distilled under reduced pressure (15–20 mmHg). The reaction products were purified by column chromatography on silica gel (220–440 mesh) eluting with methylene dichloride–acetone (95:5) and recrystallized from an acetone–water mixture.

Synthesis of tetraphenylarsonium 2-(5-methylamino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (A)

A solution of AsPh$_4$·L′ (100 mg, 0.16 mmol), CH$_3$I (0.045 cm^3, 0.72 mmol) and PS (40 mg, 0.19 mmol) in DMF (3 cm^3) was heated under nitrogen at 90 °C for 45 min. After reaching room temperature, DMF was removed under a stream of air. The residue was washed with hexane and purified by column chromatography. The second eluted fraction, showing a band maximum at 572 nm, was collected and evaporated to dryness in air. After crystallization, deep-violet crystals of AsPh$_4$·**1** (27 mg, 26%) were obtained, mp 175 °C (Found: C, 68.49; H, 3.77; N, 15.80. C$_{36}$H$_{24}$AsN$_7$ requires C, 68.68; H, 3.84; N, 15.57%); λ_{max} 576, ε_{max} 36400, hhw 79; ν_{max} 3425 (NH), 2924, 2866 (CH) and 2199 (CN); δ 7.83–7.56 (20H, m, Ph), 4.48 (1H, q, J 5.3, NH), 3.04 (3H, d, J 5.5, CH$_3$).

Synthesis of tetraphenylarsonium 2-(5-dimethylamino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (B)

A solution of AsPh$_4$·L′ (100 mg, 0.16 mmol), CH$_3$I (0.090 cm^3, 1.44 mmol) and PS (80 mg, 0.38 mmol) in DMF (3 cm^3) was heated under nitrogen at 90 °C for 1.5 h. After allowing the solution to reach room temperature, DMF was removed under a stream of air. The residue was washed with hexane and purified by column chromatography. The first eluted fraction, showing a band maximum at 597 nm, was collected and evaporated to dryness in air. After crystallization, deep-blue crystals of AsPh$_4$·**2** (23 mg, 22%) were obtained, mp 165 °C (Found: C, 68.81; H, 3.96; N, 15.16. C$_{37}$H$_{26}$AsN$_7$ requires C, 69.05; H, 4.07; N, 15.23%); λ_{max} 606, ε_{max} 30600, hhw 99; ν_{max} 2928, 2874 (CH) and 2196 (CN); δ 7.87–7.55 (20H, m, Ph), 3.16 (6H, s, CH$_3$).

Synthesis of tetraphenylarsonium 2-(5-benzylamino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (C)

To a solution of AsPh$_4$·**6** (1.0 g, 1.42 mmol) and NaBH$_3$CN (180 mg, 2.86 mmol) in EtOH (30 cm^3), CH$_3$COOH (0.165 cm^3, 2.86 mmol) was added. The color turned immediately from red to violet. After stirring for 10 min under nitrogen at room temperature, the solution was evaporated to dryness in air. The residue was purified by column chromatography using a CH$_3$Cl–acetone (80:20) eluent mixture. The first eluted fraction, showing a band maximum at 571 nm, was collected and evaporated to dryness in air. After crystallization, deep-violet crystals of AsPh$_4$·**3** (0.6 g, 60%) were obtained, mp 150 °C (Found: C, 71.31; H, 3.93; N, 13.89. C$_{42}$H$_{28}$AsN$_7$ requires C, 71.49; H, 4.00; N, 13.89%); λ_{max} 574, ε_{max} 34400, hhw 76; ν_{max} 3337 (NH), 2924 (CH) and 2196 (CN); δ 7.84–7.55 (20H, m, PhAs), 7.40–7.18 [5H, m, C$_6$H$_5$ (PhC)], 4.75 (1H, t, J 5.3, NH) and 4.61 (2H, d, J 5.9, CH$_2$).

Synthesis of tetraphenylarsonium 2-(5-dimethylaminomethylene-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (D)

To a solution of AsPh$_4$·L′ (100 mg, 0.16 mmol) in THF (3 cm^3), *N,N*-dimethylformamide diethyl acetal (0.05 cm^3, 0.29 mmol) was added under nitrogen at room temperature. After stirring for 1 h at 80 °C the reaction went to completion. Then, the solution was evaporated to dryness in air and the residue recrystallized. Deep-violet crystals of AsPh$_4$·**4** (90 mg, 82%) were obtained, mp 190 °C (Found: C, 67.90; H, 4.02; N, 16.65. C$_{38}$H$_{27}$AsN$_8$ requires C, 68.06; H, 4.05; N, 16.70%); λ_{max} 579, ε_{max} 31600, hhw 94; ν_{max} 2928, 2871, 2809 (CH) and 2203 (CN); δ 8.49 (1H, s, CH), 7.85–7.57 (20H, m, Ph) and 3.05 (6H, s, CH$_3$).

Synthesis of tetraphenylarsonium 2-(5-propylaminocarbonyl-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide (E)

A solution of AsPh$_4$·L′ (1.0 g, 1.42 mmol), PrNCO (1.6 cm^3, 16.8 mmol), triethylamine (1.25 cm^3) in DMF (30 cm^3) was heated for 4.5 h at 80 °C under nitrogen. Then the solution was evaporated to dryness in air. The residue, after washing with hexane, was purified by column chromatography. The eluted fraction, showing a band maximum at 532 nm, was collected and evaporated to dryness in air. After crystallization, deep-red crystals of AsPh$_4$·**5** (0.26 g, 23%) were obtained, mp 175 °C (Found: C, 66.65; H, 4.08; N, 15.78. C$_{39}$H$_{29}$AsN$_8$O requires C, 66.96; H, 4.17; N, 15.99%); λ_{max} 532, ε_{max} 41200, hhw 63; ν_{max} 3323 [NH (L′)], 3292 [NH (propyl)], 2966, 2924, 2870 (CH) and 2207 (CN); δ 8.84 [1H, t, *J* 4, NH (propyl)], 7.88–7.55 (20H, m, Ph), 6.74 [1H, s, NH (L′)], 3.25 (2H, m, CH$_2$), 1.57 (2H, m, CH$_2$) and 0.87 (3H, t, *J* 7.4, CH$_3$).

X-Ray crystallography

General. Three-dimensional X-ray data from suitable crystals of the tetraphenylarsonium salts of the title anions were collected in the range $4° \leq 2\theta \leq 124°$ on a Rigaku four-circle diffractometer equipped with a rotating anode (Cu-Kα radiation) by the θ–2θ scan method. Data were corrected for Lorentz and polarization effects and for absorption by semi-empirical ψ-scan method. All the structures were solved by direct methods using the SIR97 package of crystallographic programs [22] and refined by full-matrix least-squares methods with the SHELXTL programs.[23] Hydrogen atoms were included in calculated positions and refined in riding mode. CCDC reference number 207/486. See http://www.rsc.org/suppdata/p1/b0/b003407j/ for crystallographic files in .cif format.

Compound A. Crystal data: C$_{36}$H$_{24}$AsN$_7$, $M = 629.5$, crystallizes as violet irregular platelets; crystal dimensions $0.4 \times 0.4 \times 0.02$ mm, monoclinic, $a = 9.458(1)$, $b = 13.658(2)$, $c = 23.889(4)$ Å, $\beta = 94.47(1)°$, $U = 3076.5(8)$ Å^3, space group $P2_1/n$, μ(Cu-Kα) = 1.941 mm^{-1}, $T = 293$ K, $Z = 4$, $\rho = 1.36$ g cm^{-3}, final conventional $R = 0.054$ and $R_w = 0.066$ for 2765 unique reflections with $F_o \geq 6\sigma(F_o)$. Goodness of fit = 1.43.

Compound B. Crystal data: C$_{37}$H$_{26}$AsN$_7$, $M = 643.6$, crystallizes as bronze hexagonal platelets; crystal dimensions $0.4 \times 0.4 \times 0.01$ mm, monoclinic, $a = 12.707(3)$, $b = 15.364(5)$, $c = 17.717(2)$ Å, $\beta = 104.38(1)°$, $U = 3273(1)$ Å^3, space group $P2_1/n$, μ(Cu-Kα) = 1.856 mm^{-1}, $T = 293$ K, $Z = 4$, $\rho = 1.32$ g cm^{-3}, final conventional $R = 0.065$ and $R_w = 0.087$ for 3845 unique reflections with $F_o \geq 8\sigma(F_o)$. Goodness of fit = 0.92.

Compound D. Crystal data: C$_{38}$H$_{27}$AsN$_8$, $M = 670.6$, crystallizes as red-violet needles; crystal dimensions $0.4 \times 0.05 \times 0.03$ mm, monoclinic, $a = 9.557(1)$, $b = 13.607(3)$, $c = 25.454(5)$ Å, $\beta = 92.35(2)°$, $U = 3307(1)$ Å^3, space group $P2_1/n$, μ(Cu-Kα) = 1.849 mm^{-1}, $T = 293$ K, $Z = 4$, $\rho = 1.35$ g cm^{-3}, final conventional $R = 0.068$ and $R_w = 0.107$ for 3004 unique reflections with $F_o \geq 6\sigma(F_o)$. Goodness of fit = 1.00.

Compound E. Crystal data: C$_{39}$H$_{29}$AsN$_8$O, $M = 700.6$, crystallizes as red-brown thin platelets; crystal dimensions $0.6 \times 0.1 \times 0.02$ mm, triclinic, $a = 14.056(2)$, $b = 14.057(2)$, $c = 9.565(1)$ Å, $\alpha = 103.56(1)$, $\beta = 109.67(1)$, $\gamma = 88.65(1)°$, $U = 1726.8(9)$ Å^3, space group $P\bar{1}$, μ(Cu-Kα) = 1.817 mm^{-1}, $T = 293$ K, $Z = 2$, $\rho = 1.35$ g cm^{-3}, final conventional $R = 0.044$ and $R_w = 0.065$ for 4442 unique reflections with $F_o \geq 4\sigma(F_o)$. Goodness of fit = 1.05.

References

1 A. Flamini and N. Poli, *US Patent*, 1992, 5151527; G. Dessy, V. Fares, A. Flamini and A. M. Giuliani, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 426.
2 M. Bonamico, V. Fares, A. Flamini and N. Poli, *Inorg. Chem.*, 1991, **30**, 3081.
3 M. Bonamico, V. Fares, A. Flamini and N. Poli, *J. Chem. Soc., Dalton Trans.*, 1992, 3273.
4 M. Bonamico, V. Fares, A. Flamini, N. Poli and G. Mattei, *Polyhedron*, 1993, **12**, 1209.
5 M. Bonamico, V. Fares, A. Flamini and N. Poli, *J. Chem. Soc., Dalton Trans.*, 1993, 2073.
6 V. Fares, A. Flamini, J. R. Jasin, R. L. Musselman and N. Poli, *J. Chem. Soc., Dalton Trans.*, 1995, 281.
7 K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1659.
8 C. B. Hoffman, V. Fares, A. Flamini and R. L. Musselman, *Inorg. Chem.*, 1999, **38**, 574.
9 A. Panusa, A. Flamini and N. Poli, *Chem. Mater.*, 1996, **8**, 1202.
10 V. Fares, A. Flamini, D. Capitani and R. Rella, *J. Mater. Chem.*, 1998, **8**, 1139.
11 A. Flamini, G. Mattei and A. Panusa, *J. Inclusion Phenom.*, 1999, **33**, 377.
12 V. N. Kopranekov, L. S. Gorcharova and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1979, **49**, 1408.
13 H. Z. Sommer and L. L. Jackson, *J. Org. Chem.*, 1970, **35**, 1558; H. Z. Sommer, H. I. Lipp and L. L. Jackson, *J. Org. Chem.*, 1971, **36**, 824.
14 V. Fares, A. Flamini and N. Poli, *J. Chem. Res. (S)*, 1995, 228; V. Fares, A. Flamini and N. Poli, *J. Chem. Res. (M)*, 1501.
15 A. Novak, *Struct. Bonding (Berlin)*, 1974, **18**, 177.
16 V. Fares, A. Flamini and N. Poli, *J. Chem. Res. (S)*, 1995, 494; V. Fares, A. Flamini and N. Poli, *J. Chem. Res. (M)*, 3054.
17 P. F. Gordon and P. Gregory, *Organic Chemistry in Colour*, Springer Verlag, Heidelberg, 1983, p. 239.
18 A. Ansorge, D. J. Brauer, B. Krum and G. Pawelke, *J. Organomet. Chem.*, 1993, **446**, 25.
19 C. D. Keating, M. D. Musick, M. H. Keefe and M. J. Natan, *J. Chem. Educ.*, 1999, **76**, 949.
20 F. Baldini, A. Falai, A. Flamini, P. Pasetto and A. Mencaglia, *Quimica Analitica*, 2000, **19**, 105.
21 F. Baldini, A. Falai, A. Flamini, P. Pasetto and A. Mencaglia, unpublished work.
22 A. Altomare, M. C. Burla, C. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
23 G. M. Sheldrick, *SHELXTL*, Siemens, Madison, WI, 1996, vol. 5.