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Communications to the Editor

Reductive Condensation of Tetracyanoethylene on a Metal Center. Synthesis and Characterization of 5-Amino-3-imino-1,2,6,7-tetracyano-3*H*-pyrrolizine

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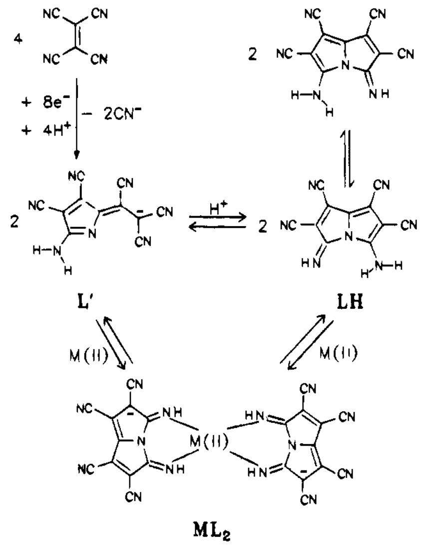
Some years ago we discovered[1] and patented[2] the reductive condensation of four tetracyanoethylene molecules on a metal center in the form of two pyrrolizinato moieties (L) by a two-step procedure, as outlined in Scheme 1.

The overall reaction may be regarded as the missing element in the series of formation reactions of conjugated macrocycles starting with polycyano-substituted ethylenes. In fact, *cis*-1,2-dicyanoethylenes, under the appropriate conditions, undergo reductive cyclotetramerization around a metal center yielding the metal−tetraazaporphyrins, MTAP[3] (metal−phthalocyanines, MPc, are similarly produced from 1,2-dicyanobenzenes[4]). Also, tricyanoethylenes are converted to the corresponding metal−tetracyanotetraazaporphyrins, MTAP(CN)$_4$, by the same method.[5] By contrast, tetracyanoethylene seems not to tolerate reductive cyclotetramerization, and consequently, no reports have appeared on the hypothetical MTAP(CN)$_8$, despite great interest in tetrapyrrole macrocycles. Thus, we have carried out an extensive investigation on the species L′, ML$_2$, and LH.

Uncoordinated L′ ($C_{11}N_7H_2^-$), which can be prepared by a high-yield, gram-scale reaction,[2] exists as the 2*H*-pyrrolyl anion;[6] the sodium salt is very stable and soluble in water, while the tetraphenylarsonium salt is soluble in organic solvents.[7]

ML$_2$ are species of prospective use in materials chemistry because they have an electronic structure similar to that of MPc's[8] and may serve as functional dyes or stacking compounds. The stack-forming properties may be enhanced in ML$_2$ as compared to MPc, by the intermolecular interaction associated with the CN groups.[9] However, ML$_2$ species have not revealed the expected stack-forming properties, because of the crystallization solvent always present in the solid state, which prevents close packing, being hydrogen bonded to the imino groups in the molecular plane and/or apically coordinated to the metal.[10] Furthermore, sublimation attempts to deposit ML$_2$ as solvent-free species have been unsuccessful, given their thermal instability at high temperature. Thus it was of interest to isolate and characterize the conjugated acid $C_{11}N_7H_3$ (LH), since we knew that such species can be sublimed. The acids LH have also been identified by mass spectroscopy during the characterization of L′.[11]

Scheme 1



LH is readily obtained as a water-free microcrystalline powder on acidification of NaL′ (L′ + H$^+$ → LH).[12] As in the formation of the β-diiminopyrrolizinide from L′ on coordination to metal(II) cations,[1] the final protonation site is the nitrile nitrogen atom adjacent to the pyrrolic nitrogen atom of L′ and the intramolecular condensation leading to the pyrrolizine nucleus is attained through 3,4-bond formation.

The X-ray diffraction analysis of LH was undertaken on a single crystal of its 2:1 1-chloronaphthalene (NAPH) adduct.[13] The structure consists of coplanar units of LH and NAPH lying approximately in the (2 0 4) planes. In each plane, hydrogen-bonded, symmetry-related (centrosymmetrically coupled and *b*-shifted) LH units are arranged in parallel rows, which are separated by centrosymmetrical, highly disordered,[14] discrete units of NAPH. An interplanar distance of 3.39 Å, involving superposed LH and NAPH units, is observed. In spite of the presence of disordered NAPH in the cell, the molecular structure of the LH is well defined (Figure 1). The amino and imino hydrogen atoms are clearly located by a Fourier difference map. In comparison with the ML$_2$ metal complexes, where L shows

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[12] To a solution of NaL′ (0.24 g, 0.94 mmol) in water (40 mL) was added dropwise concentrated HCl (2 mL). A golden microcrystalline precipitate formed, which was filtered off, washed with water, and dried (0.21 g, 95% yield). Anal. Calcd for $C_{11}H_3N_7$: C, 56.65; H, 1.30; N, 42.05. Found: C, 56.90; H, 1.29; N, 41.01.

[13] Crystal data for $C_{11}N_7H_3 \cdot {}^1/_2C_{10}H_7Cl$: red brown irregular prisms, monoclinic, $P2_1/n$, $a = 13.119(2)$ Å, $b = 8.911(1)$ Å, $c = 13.548(3)$ Å, $\beta = 104.02(1)°$, $V = 1536.6(1)$ Å^3, $Z = 4$, $R = 0.078$, $R_w = 0.102$, $s = 1.38$, Siemens R3m diffractometer, 3852 measured reflections, Mo Kα, 3489 independent ($R_{int} = 0.026$), 1324 observed reflections [$I > 3\sigma(I)$]. Suitable crystals were grown in a sealed vial from a saturated hot solution of 1,2-dichlorobenzene and 1-chloronaphthalene (1:1), by slow cooling from 140 °C to room temperature over 6 days. Anal. Calcd for $C_{32}H_{13}ClN_{14}$: C, 61.10; H, 2.08; N, 31.17. Found: C, 61.57; H, 2.08; N, 31.18. IR: $\nu_{NAPH} = 802$ and 774 cm^{-1}.

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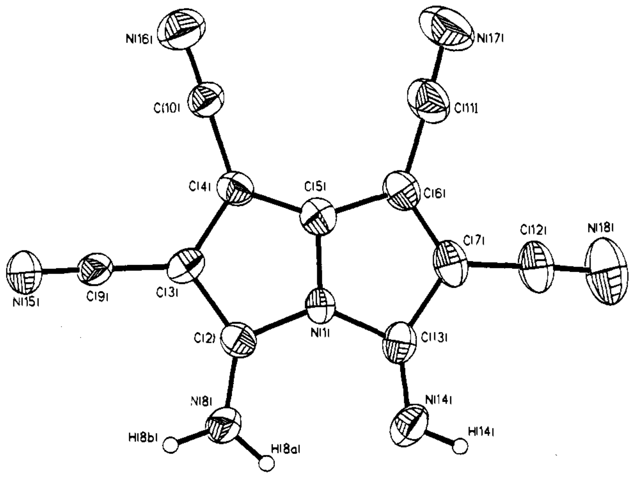

Figure 1. Structure of $C_{11}N_7H_3$. Important bond lengths (Å): N(1)−C(2) 1.400(6), N(1)−C(5) 1.364(7), N(1)−C(13) 1.412(6), C(2)−C(3) 1.393(7), C(2)−N(8) 1.305(7), C(3)−C(4) 1.429(7), C(4)−C(5) 1.273(7), C(5)−C(6) 1.431(7), C(6)−C(7) 1.364(9), C(7)−C(13) 1.470(8), C(13)−N(14) 1.268(8).

an extensive conjugation within the condensed rings, in the LH there is a significant localization of the double bonds. Only one of the two possible tautomeric forms is therefore present in the solid state.

LH is very soluble and stable in dry hydrogen-bonding solvents; water reverses its formation reaction.[15] In solution it is best described by the two degenerate tautomers due to fast N−H proton exchange, as revealed by its ^{13}C-NMR spectrum. From room temperature down to −30 °C it shows five fairly sharp peaks,[16] simulating a symmetric (C_{2v}) pyrrolizine from which six carbon resonances are expected or fewer for accidental degeneracy as in ML_2, *i.e.*, six resonances from ZnL_2[1] or four resonances from PdL_2.[10b] Its optical spectrum is significantly different from that of L′.[17] Moreover, LH is fluorescent in solution,[18] in marked contrast to L′, which is not fluorescent at all. A large quenching effect is observed on the fluorescence of LH from species more basic than it, water included. The effect of deuterium substitution of the hydrogen[19] on the fluorescence yield at room temperature has been examined also. Such an effect has been found to be negligible within experimental error.[20] LH reacts with MCl_2 (M = Fe, Co, Ni, Cu) even in heterogeneous phases, readily giving ML_2 in high yield.[21] More importantly, LH sublimes, affording thickness-controlled thin films that show a fairly high degree of crystalline order.[22] The optical spectrum of an evaporated film in comparison with the solution spectrum shows strong intermolecular interaction to occur in the solvent-free solid state phase.[23] In addition, the film exhibits an electrical dark conductivity ($\sigma = 4.7 \times 10^{-9}$ S cm^{-1}),[24] a value typical of evaporated organic layers,[25] and in particular of H_2Pc ($\sigma = 10^{-9}$ S cm^{-1}).[26]

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Supporting Information Available: Crystallographic information including data collection, refinement details, bond distances and angles, atomic coordinates and thermal parameters, and drawings of crystal packing and disordered NAPH unit (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[15] This is evident from the change of the solution optical spectrum of LH in anhydrous THF on adding water: the spectrum of L′ is quantitatively obtained.[17]

[16] ^{13}C NMR spectra were recorded on a Bruker AMX-600 spectrometer operating at 150.9 MHz, in a THF-d_8/THF solution: 108.79, 110.35, 124.85, 127.83, 150.48 ppm from TMS.

[17] UV/vis: LH (λ_{max} = 580, E_{580} = 20 000), L′ (λ_{max} = 560 nm E_{560} = 35 000 M^{-1} cm^{-1}).

[18] Fluorescence spectra were recorded on a Perkin-Elmer MPF-44B spectrometer: solvent, THF; λ_{em} = 640 nm; λ_{ex} = 480 nm; φ = 0.35 (fluorescence quantum yield, rhodamine-B as quantum counter).

[19] LH is rapidly and fully deuterated in the solid state simply on exposure to D_2O vapor, as indicated by the IR frequency shift of the pertinent bands: ν_{N-H} 3240 (Nujol mull) and 3575 (THF solution), ν_{N-D} 2385 and 2300 cm^{-1}, respectively. Samples prepared in drybox.

[20] The fluorescence quantum yield of $C_{11}N_7D_3$ in THF at room temperature is 0.95 relative to $C_{11}N_7H_3$.

[21] Anhydrous MCl_2 (M = Fe, Co, Ni, Cu) was added to a THF (dried and freshly distilled) solution of LH (7 × 10^{-4} M). A rapid quantitative reaction occurred as indicated by absorbance measurements at the highest peak wavelength (nm): Fe (616), Co (642), Ni (674), Cu (659).

[22] Thin films (200−800 nm) were grown (T_{subl} = 200 °C, 10^{-6} mmHg) in an Edwards Auto 306 vacuum coater, equipped with a quartz thickness monitor. Their X-ray diffraction spectra consist of a single, well-defined peak at d = 3.17 Å, superimposed on a slightly amorphous pattern.

[23] The visible spectrum of the sublimed film shows an extra band in comparison to the solution spectrum[17] (maxima at 612 and 572 nm (E_{612} = 19 000 M^{-1} cm^{-1}, E_{572} = 20 000 M^{-1} cm^{-1}), originated probably either by the Davidov splitting of the single-molecule HOMO → LUMO transition or by an intermolecular charge transfer transition.

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