

Electrosynthesis of a Stable Delocalized Carbanion: Potassium and Ammonium Salts of *p*-Cyanophenyl Malononitrile

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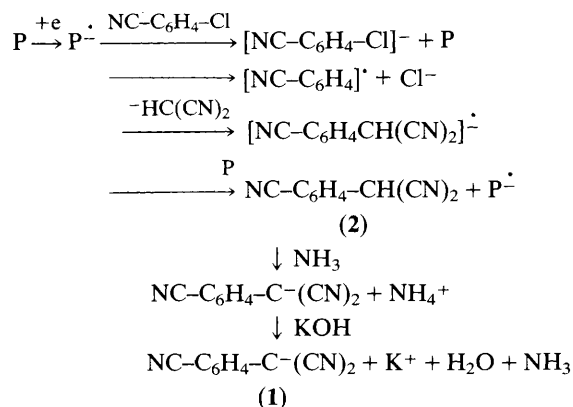
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The air stable potassium and ammonium salts of *p*-cyanophenyl malononitrile have been prepared by a one-pot reaction with very high yield.

In the synthesis of semi-conducting crystals, principally in the series of tetrathiafulvalene (TTF) or its derivatives, most counter-anions are inorganic species such as Cl^- , PF_6^- , ClO_4^- , MX_4^{2-} etc.; organic anions are rather unusual. Beside the earliest known tetracyanoquinodimethane (TCNQ) anion reported for the complex TTF-TCNQ¹ few examples of stable organic mono- and di-anions have been mentioned in the literature.² Among them *p*-nitrophenyl malononitrile was recently reported to give charge transfer (CT) complexes with TTF and tetramethyltetraselenafulvalene (TMTSF).³

In the search for planar organic anions of small size and high polarizability which could engage in a reaction with an organic cation radical such as TTF^+ or its derivatives we found a simple method to prepare a salt of *p*-cyanophenyl malononitrile (**1**). Several attempts to achieve a direct nucleophilic aromatic substitution of *p*-chloro benzonitrile by malononitrile carbanion have failed. Some years ago, Arnett⁴ mentioned a four-step synthesis of the potassium salt (**1**) using cyanogen halides and *p*-cyanophenyl acetonitrile as reagents. Here we report a one-pot electrochemical synthesis of this product with very high yield.†

† Electrochemical reaction was carried out in a 100 ml cell with a 0.5 mm smooth gold rod for the working electrode, a Pt grid (1024 mesh/cm²) for the counter electrode, and a Ag^+/Ag electrode for voltammogram recording. Reagents were introduced, in liquid ammonia at -40°C , in the following order: i, 0.02 M 4,4'-bipyridine; ii, 0.08 M *p*-chlorobenzonitrile (saturated solution); iii, 0.33 M K and malononitrile; iv, 0.06 M KOH at the final state. The reaction was complete after a transfer of 0.3 F/mol of *p*-chlorobenzonitrile with a current density of 2.5 mA/cm². After complete evaporation of ammonia the solid residue was dissolved in 100 ml of CH_2Cl_2 and washed with water. The organic solution was evaporated to dryness and the salt purified by reflux with charcoal in acetone. The salt precipitated by adding ether to the concentrated previous solution.



The benzonitrile radical ($\text{NC-C}_6\text{H}_4$)[·] produced *in situ* via reductive cleavage of *p*-chlorobenzonitrile reacts according to an $\text{S}_{\text{NR}}1$ mechanism with excess of malononitrile carbanion to give the salt of *p*-cyanophenyl malononitrile (**1**). The presence of a small amount of 4,4'-bipyridine (P) as mediator (10–20 mol%) combined with a relatively 'low' current density (*i.e.*, 1.5–2.5 mA/cm² on a platinum grid for a solution of 0.08 M *p*-chlorobenzonitrile in liquid ammonia) improved the yield to over 85%.⁵ The mediator plays a key role as initiator of the benzonitrile radical and as an indicator of the end of the reaction.

The reaction course was followed by the observation of the completely reversible equilibrium of the mediator in the corresponding cyclic voltammogram. After complete evaporation of ammonia the product was isolated as the potassium salt (**1**).

Contrary to previous reports⁴ the potassium salt is stable in air and can be recrystallised from organic solvents (acetone–

Table 1. ^{13}C NMR chemical shifts (ppm).

	Acid (2)	Carbanion (1)
Methylidene	28.6	34.3
Nitrile	113.2	97.8
Aromatic	133.8	149.7

ether). When treated with concentrated hydrochloric acid and extracted with ether one can obtain the protonated form (2). Triethylamine reacts with the 'acid' (2) to yield the stable corresponding ammonium salt. Alkyl halides such as methyl iodide or octadecyl iodide react with the salt (1) to give only C-alkylation products.

The carbanion (1) exhibits a reversible reduction with $E^\circ -2.135\text{ V}$ (vs. Ag^+/Ag as reference electrode); in contrast, upon oxidation, the salt (1) gives a non reversible wave at $E_{\text{pA}} + 0.43\text{ V}$ [vs. standard calomel electrode (SCE) in MeCN].

The electronic UV-VIS spectrum of the salt (1) exhibits two strong absorption bands in acetonitrile at 355 ($\epsilon\ 3 \times 10^4$) and 225 nm ($\epsilon\ 1.2 \times 10^4$) attributed to the benzene ring. The IR spectrum, recorded in the transmission mode, shows three CN stretching bands at 2209, 2178, and 2143 cm^{-1} (compared to the single peak of the corresponding acid at 2237 cm^{-1}) which probably indicates a non-planar structure of the anion.

The ^1H NMR spectrum of the salt (1) in $(\text{CD}_3)_2\text{CO}$ exhibits an aromatic quadruplet AA'BB' located at $\delta\ 6.86\text{--}7.23$ (J_{AB}

8.7 Hz) characteristic of *p*-disubstituted benzene whereas the 'acid' form (2) presents a quadruplet at $\delta\ 7.9\text{--}8.0$ ($J_{\text{AB}}\ 9\text{ Hz}$). The ^1H NMR spectrum shows therefore that the negative charge could be partially delocalized through the ring onto the single nitrile group to give a quinoid structure.

However, the ^{13}C NMR spectroscopic data suggest that the delocalization of the negative charge occurs on the two terminal nitrile groups; the evidence of this magnetic shielding is shown in Table 1. The difficulty in assigning the ^{13}C chemical shifts does not allow us to quantify this delocalization, and so further investigations are necessary.

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