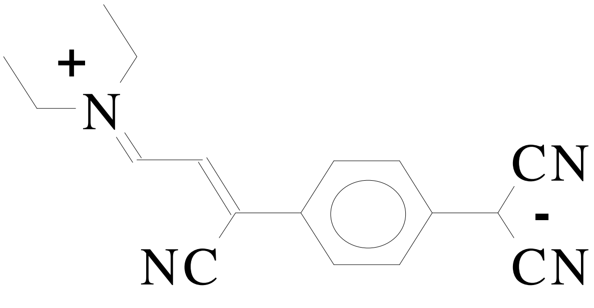
## *Abstract*

# Novel Reactions of TCNQ:- Formation of Zwitterions for Nonlinear Optics by Reaction with Enamines.

Marek Szablewski

Hitherto unreported reactions of enamines with the strong π acid 7,7,8,8-tetracyanoquinodimethane (TCNQ) have led to the formation of novel zwitterionic materials of significant importance for nonlinear optics. TCNQ has been found to react in an analogous manner to chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) with tertiary amines, abstracting protons from triethylamine to form an enamine. Subsequent reaction of the enamine with TCNQ is thought to proceed *via* a Stork enamine process. TCNQ, a highly conjugated nitrile, acts as a Michael acceptor to generate a zwitterionic product (**1**). Enamines can also be generated *in situ* by the reaction of an aldehyde and a secondary amine prior to the addition of TCNQ. The highly polar zwitterions have large theoretical second order molecular hyperpolarisabilites and may be of interest in nonlinear optical applications, especially in frequency doubling of laser light for blue light generation.



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# Novel Reactions of TCNQ:- Formation of Zwitterions for Nonlinear Optics by Reaction with Enamines.

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*Summary:-* Zwitterionic adducts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been synthesised by the action of enamines on TCNQ.

TCNQ has been known[1] since 1960 and there can be few organic molecules which have attracted a more active research effort. The chemistry of TCNQ has in consequence been well documented.[2,3]

Primarily due to its high electron affinity[4] ($E_A$= 2.84 eV) TCNQ **1** forms stable charge transfer salts whose electrical conductivity range from insulating to metallic with a variety of inorganic and organic electron donors.

Substitution reactions of TCNQ with primary and secondary amines[5] yield products in which either one or two cyano groups are replaced by the amino moiety (Scheme **I**). The amine group adds to the TCNQ through the nitrogen in the manner of a 1,6 addition yielding a product which subsequently eliminates HCN resulting in a mono- or bi-amino substitution product. Mixed derivatives of TCNQ have been prepared in a similar manner by the reaction of a mono-amine substituted TCNQ with an excess of another, different amine, whereas bi-functional amines such as 1,2-diaminoethane can replace both nitrile groups at one end of a TCNQ molecule to yield a cyclic product.

Tertiary amines such as triethylamine (TEA) are not expected to react with TCNQ as they do not possess an amino hydrogen which could be abstracted to produce the expected 1,6 addition intermediate. Indeed the reaction of TEA with TCNQ in acetonitrile[1] or THF[2] has become the common method of preparing the "complex" or 1:2 radical anion salt $Et_3NH^+(TCNQ)(TCNQ^-)$. The mechanism of the salt formation is not fully understood in this case as the source of the ammonium proton is not satisfactorily established. It has however been postulated[2] that the proton is derived from the amine. Facile deprotonation of TEA in the presence of a strong electron acceptor, 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) **2** ($E_A$= 1.35 eV)[4] yielding an enamine **3** has been observed during the formation of the blue substituted chloroquinone **4** (Scheme **II**).[6,7,8] In the reaction sequence illustrated in Scheme **II**, it is envisaged that the chloranil **4** has a twofold function. Initially one equivalent of chloranil acts as a base facilitating the abstraction of a proton from the TEA resulting in the formation of 1,4-dihydro-2,3,5,6-tetrachlorobenzene and the enamine **3.** The enamine **3** can in turn react with a further equivalent of chloranil, by addition of the enamine to the α,β unsaturated ketone functionality of chloranil resulting in a formal Stork enamine addition reaction.

We now report a related reaction of TEA with TCNQ in chloroform (Scheme **III**) :- to our knowledge the first reported reaction of TCNQ with a tertiary amine leading to the formation of the zwitterionic adduct **5** (DEMI-3CNQ)[9]. As in the reaction between chloranil and TEA, the electron acceptor, in this case TCNQ, abstracts protons from the TEA yielding the enamine and di-hydro TCNQ ($TCNQH_2$) **6** which has been identified in the crude reaction mixture by its characteristic peak at 317 nm in the UV/vis spectrum. Subsequent elimination of HCN from the initial addition product results in the formation of **5**. The zwitterion **5** has also been synthesised by direct reaction of TCNQ with an enamine. *In situ* enamine formation (scheme **IV**) by the reaction of diethylamine with methanal yields the same enamine as shown in scheme **II**. The enamine attacks the TCNQ a highly conjugated nitrile and hence a Michael acceptor, resulting in the zwitterionic adduct **5** which is collected after recrystallisation as green-gold lustrous needles.

The TEA reaction has been followed by monitoring UV/vis spectra of aliquots of the reaction mixture. Initially the solution has the characteristic spectrum of TCNQ with a single absorption at 395 nm. After the addition of the amine the solution exhibits a colour change from yellow to green as the TCNQ peak rapidly diminishes. At this point the spectrum is that expected of $TCNQ^-$ species with peaks at 420 and 842 nm, which could be due to the formation of $TCNQH^-$ moities, probably intermediate in the formation of $TCNQH_2$ **6** . The colour develops through turquoise to blue, accompanied by a gradual decrease in the bands at 420 and 842 nm and an increase in the charge transfer band at 698 nm.

Similarly to other zwitterionic donor-acceptor adducts of TCNQ[10]**,** **5** is characterised by a very distinctive broad charge transfer absorption band in the UV/vis spectrum. In contrast however to the previously reported pyridinium and quinolinium zwitterions, which exhibit a single broad peak, **5** has a band with two maxima ($\lambda_{max}$ 698 nm in acetonitrile) and a slight double shoulder on the short wavelength side of the band. Very little absorbance occurs immediately on either side of these intense transitions. The infrared spectrum of **5** shows a doublet at the C=N stretching frequencies at 2185.7 & 2155 $cm^{-1}$. Such a doublet is characteristic of zwitterionic materials containing the dicyanomethanide group[10]. The structure of **5** has been unequivocally verified by X-ray crystallography[11], mass spectrometry, elemental analysis and $^1H$ NMR.

Stable enamines, such as 2-methylene-1,3,3,3-trimethylindoline and 1-piperidinocyclohexene have been reported[12,13] to react with TCNE (tetracyanoethylene) in an analogous manner to the reactions reported here between enamines and TCNQ. The product of the reaction (structure 7) between

2-methylene -1,3,3,3 trimethylindoline and TCNE is not however zwitterionic in nature but is a neutral conjugated substitution product of TCNE.

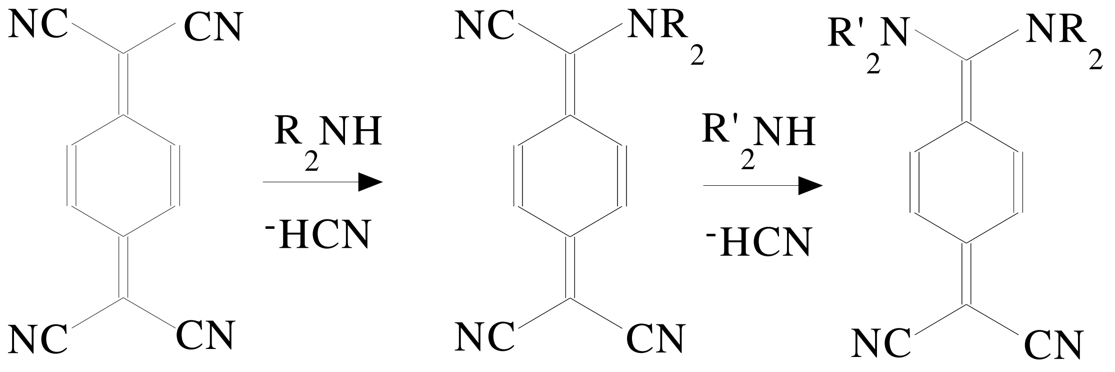
As would be expected with zwitterionic species such as **5** an extremely large dipole has been measured, $\mu = 45$ Debye ($45 \times 10^{-18}$ esu). Coupled with the large dipole moment, the large calculated molecular first hyperpolarisability, ($\beta = 300 \times 10^{-30}$ esu at 920 nm) results in a calculated value of $\mu\beta$ of $13500 \times 10^{-48}$ esu, indicating that the zwitterions may be of considerable interest in the field of nonlinear optics. Organic materials which can be used in frequency converters where phase matching is achieved using anomalous dispersion are very rare yet highly desirable[14]. Molecule **5** would be suitable for producing blue light in the range 450-470 nm from InGaAs pump sources of wavelengths between 900 and 940 nm. Such nonlinear conversion is needed for the optical data storage industry.

The simple synthetic procedures outlined above allow for the synthesis of a wide range of zwitterionic analogues of TCNQ, many of which are envisaged to possess linear and nonlinear optical properties of strategic commercial importance[15].

**Acknowledgements.**

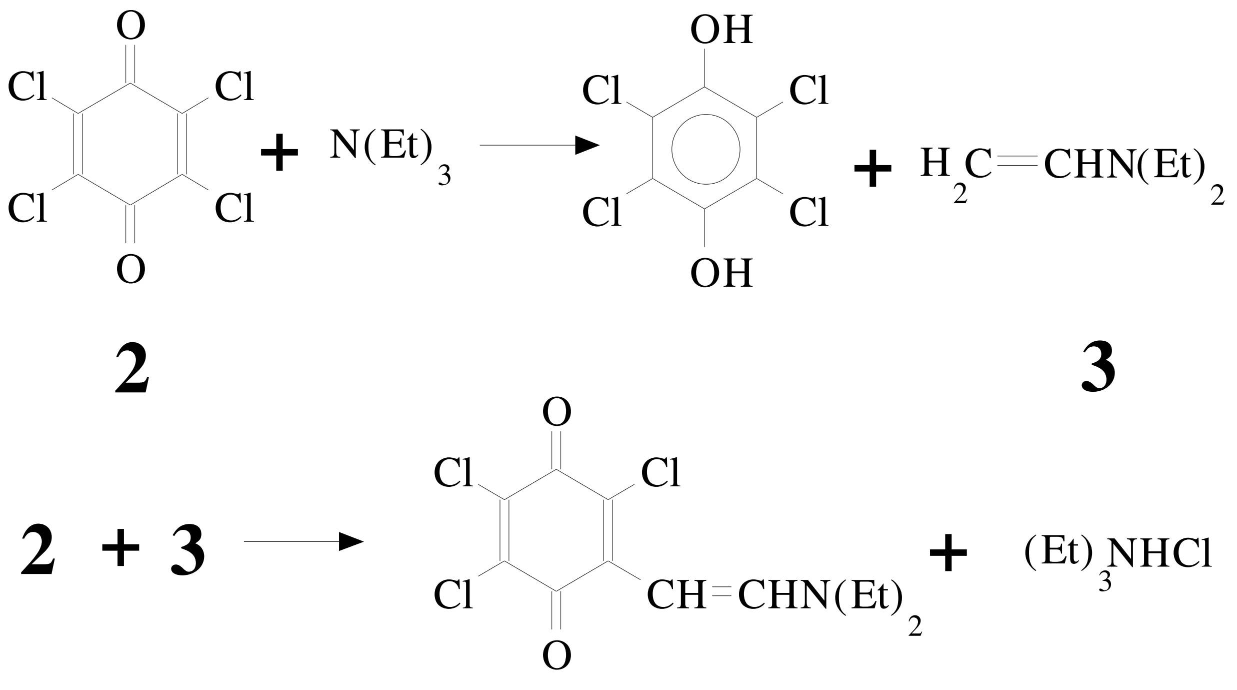
I would like to thank Dr. R.S. Matthews , Dr R. Jones, Miss L.M. Turner, Mr J. Cole and Mrs J. Dostal, all of the Chemistry Department, University of Durham for the $^1$H NMR spectrum, mass spectrum, X-ray crystal structure and elemental analysis of **5**, respectively. I would also like to thank Mr D. Gray for determining the dipole moment of **5** and Dr G.H. Cross for the theoretical calculation of the second order molecular hyperpolarisability of **5**.

## Scheme I



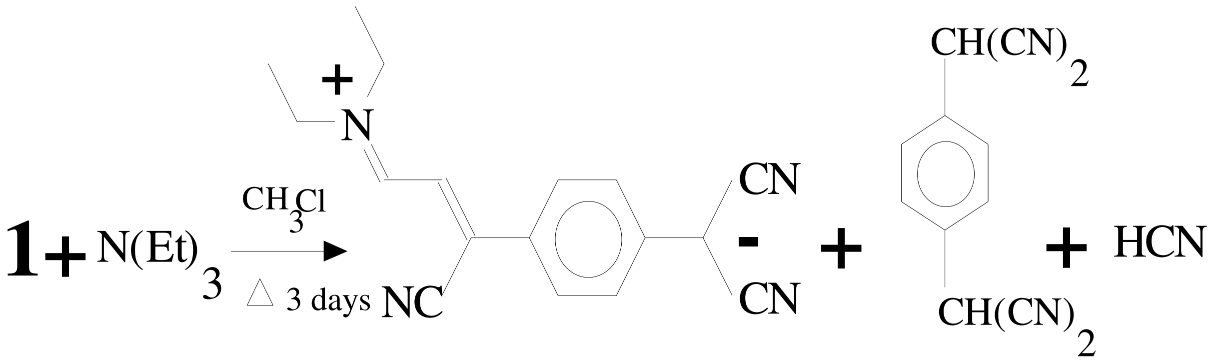
**1** R and R' = H or alkyl, R can = R'

## Scheme II



**4**

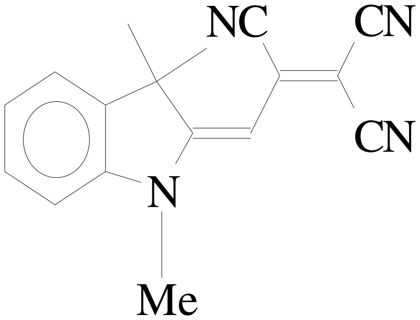
## Scheme III



**5** **6**

## Scheme IV

$$CH_3CHO + Et_2NH \xrightarrow[\triangle\ 3h,\ Na_2SO_4]{CHCl_3,\ \mathbf{1}} \mathbf{5} + H_2O + HCN$$



**7**

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## Supplementary material available:

IR, $^1$H NMR, mass spectroscopic, crystallographic, UV/vis data and preparative details are available for compound **5.** **(7 Pages)** This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS: see any current masthead page for ordering information.

# Supplementary material

## Experimental procedures.

### A. The preparation of DEMI-3CNQ, Z-β-[(N,N,diethylmethylimmonium)-α-cyano-4-styryldicyanomethanide].

A solution of TCNQ, ( 0.1 g, 0.49 mmol) in chloroform (200 mL) was heated at reflux for half an hour under nitrogen. An excess of triethylamine was added (0.5 mL , 0.363 g, 3.6 mmol) by means of a syringe. The reaction mixture was heated at reflux under nitrogen until a blue colour developed (approximately three days) whereupon the solution was removed from the heat and evaporated to dryness *in vacuo*.

The resultant solid was recrystallised from acetonitrile. The product was collected by suction filtration and washed with toluene (20 mL) and then ether (20 mL). The product DEMI-3CNQ was obtained as metallic-like green-gold needle like crystals (37 mg) 27% yield. $^1$H NMR, (DMSO), $\delta = 1.29$ ppm (dt, 6H, -$CH_3$ x 2), $\delta = 3.68$ ppm (dq, 4H, -$CH_2$- x 2), $\delta = 6.940$ & 7.77 ppm (4H, doublet of doublets, p-substituted benzene ring), $\delta = 7.36$ ppm (d , 1H, H-C=C-$\underline{\text{H}}$), $\delta = 8.27$ ppm (d , 1H, $\underline{\text{H}}$-C=C-H [proton nearest positively charged N]). Mass spectrum: m/z, $M^+$ 276. (100%, Molecular ion), Decomposition temperature 243.28 °C (determined by DSC), IR (KBr) 2185.7, 2155.6 cm$^{-1}$, (characteristic of C=N stretch in such zwitterionic species, 1588.1 cm$^{-1}$, C=N str. $\lambda_{max} = 654.4$, 698 nm. Calc. for $C_{17}H_{16}N_4$: C, 73.89; N, 20.27; H, 5.84%. Found: C, 73.83; N, 20.39; H, 5.77%.

The structure of DEMI-3CNQ was confirmed by X-ray crystallography, see attached structure and data.

B. The preparation of DEMI-3CNQ, Z-β-[(N,N,diethylmethylimmonium) -α-cyano- 4 -styryldicyanomethanide] (via *in situ* enamine formation).

Diethylamine (0.179 g, 0.253 mL, 2.45 mmol) was stirred under nitrogen in chloroform (150 mL) at room temperature with an excess of anhydrous sodium sulphate for half an hour.

Subsequently acetaldehyde (0.107 g, 0.137 mL 2.45 mmol) was added dropwise as a solution in chloroform (10 mL). The solution was stirred with gentle heating for 40 mins and then a solution of TCNQ (0.5g, 2.45 mmol) in warm chloroform (175 mL) was added dropwise. The reaction mixture was stirred with heating for a further 30 mins. During this time the reaction mixture exhibited a colour change from yellow to green. On heating the reaction mixture under reflux and under nitrogen for a further 3 hours, the colour changed to turquoise and finally to blue. A UV/vis absorption spectrum of the reaction mixture showed the characteristic peaks associated with DEMI-3CNQ. The blue solution was removed from the heat and filtered under gravity to remove sodium sulphate from the reaction mixture. The filtrate was evaporated to dryness *in vacuo*. The resultant solid was recrystallised from hot acetonitrile. The product was collected by filtration under suction and washed with toluene (20 mL) and then ether (20 mL). The product DEMI-3CNQ was obtained as metallic-like green-gold needle-like crystals (110 mg) 16 % yield. IR (KBr) 2185.7, 2155.6 cm$^{-1}$, (characteristic of C=N stretch in such zwitterionic species, $\lambda_{max}$ in acetonitrile solution = 698 nm.

## Enclosures

1. Crystal Structure of **5.**
2. IR (KBr) spectrum of **5.**
3. Mass Spectrum of **5.**
4. $^1$H NMR (DMSO) spectrum of **5.**

5. UV/vis absorption spectrum of **5** in MeCN.

2. IR (KBr) spectrum of **5.**

## 5. UV/vis absorption spectrum of **5** in MeCN.