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 synthesized by the action of enamines on TCNQ.

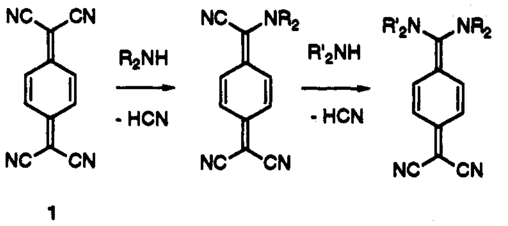
TCNQ has been known[1] since 1960, and there are few organic molecules which have attracted a more active research effort. As a consequence, the chemistry of TCNQ has been well documented.[2,3]

Primarily due to its high electron affinity[4] (E_A = 2.84 eV), TCNQ (1) forms stable charge-transfer salts whose electrical conductivity ranges 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 1). 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 bis-amino substitution product. Mixed derivatives of TCNQ have been prepared in a similar manner by the reaction of a monoamine-substituted TCNQ with an excess of another, different amine, whereas bifunctional amines such as 1,2-diaminoethane can replace both nitrile groups at one end of a TCNQ molecule to yield a cyclic product.

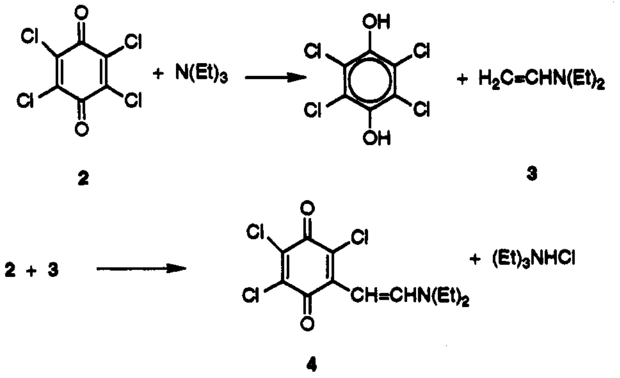
Tertiary amines such as triethylamine (TEA) are not expected to react with TCNQ as they do not possess an amino hydrogen which could be abstracted to produce the expected 1,6 addition intermediate. Indeed, the reaction of TEA with TCNQ in acetonitrile[1] or THF[2] has become the common method of preparing 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 2).[6-8] In the reaction sequence illustrated in Scheme 2, it is envisaged that the chloranil 4 has a 2-fold function. Initially, 1 equiv 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.

Scheme 1

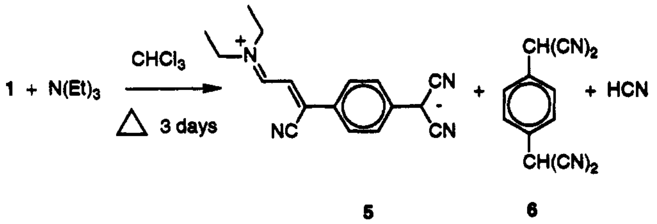


R and R' = H or alkyl, R can = R'

Scheme 2



Scheme 3



Scheme 4

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

We now report a related reaction of TEA with TCNQ in chloroform (Scheme 3; to our knowledge this 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 dihydro TCNQ ($TCNQH_2$) 6 which has been identified in the crude reaction mixture by its characteristic peak at 317 nm in

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[•] Abstract published in *Advance ACS Abstracts,* February 15, 1994.

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(9) U.K. Patent applied for 16th Oct 1993. Application No. 9321400.5.

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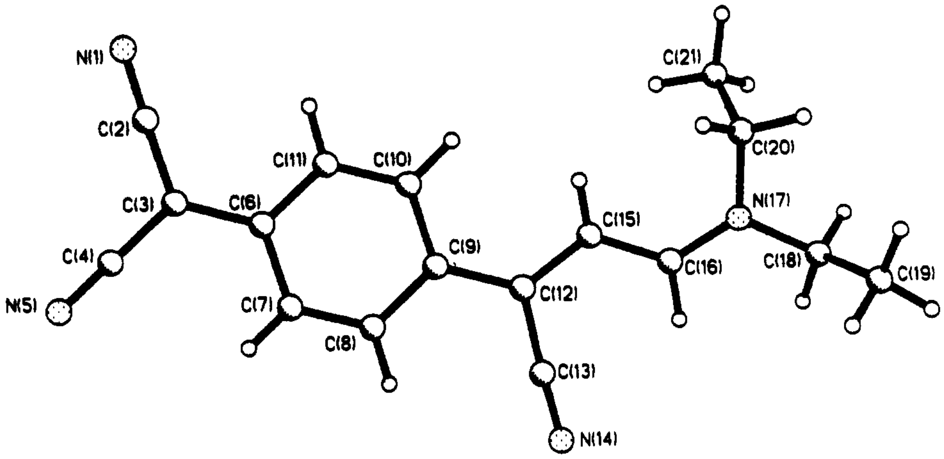


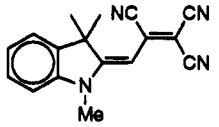
Figure 1. X-ray crystal structure of 5.

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 synthesized by direct reaction of TCNQ with an enamine. *In situ* enamine formation (Scheme 4) by the reaction of diethylamine with methanal yields the same enamine as shown in Scheme 2. The enamine attacks the TCNQ (a highly conjugated nitrile and, hence, a Michael acceptor) resulting in the zwitterionic adduct 5 which is collected after recrystallization 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 color 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 color 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 characterized 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 (λ_{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 $C\equiv N$ stretching frequencies at 2185.7 and 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] (see Figure 1), 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.



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As would be expected with zwitterionic species such as 5, an extremely large dipole has been measured, $\mu = 45$ D (45×10^{-18} esu). Coupled with the large dipole moment, the large calculated molecular first hyperpolarizability, ($\beta = 300 \times 10^{-30}$ esu at 920 nm) results in a calculated value of $\mu\beta$ of $13\,500 \times 10^{-48}$ 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]

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[10] Ashwell, G. J.; Dawnay, E. J. C.; Kuczyński, A. P.; Szablewski, M.; Sandy, I. M.; Bryce, M. R.; Grainger, A. M.; Hasan, M. *J. Chem. Soc., Faraday Trans.* **1990**, *86* , 1117.

[11] Full details of the crystal structure of 5 are given in: Cole, J.; Cross, G. H.; Howard, J. A. K.; Szablewski, M. Submitted to *Acta Crystallogr. B.*

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for determining the dipole moment of 5 and Dr. G. H. Cross for the theoretical calculation of the second-order molecular hyperpolarizability of 5.

Supplementary Material Available: General experimental procedure, characterization data, and ^{1}H NMR and UV spectra of 5 (4 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.