

Characterization of Certain *Ortho* Substituted Phenols Using Tetracyanoethylene *

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It is demonstrated that tetracyanoethylene (TCNE) is useful for the characterization of certain monohydric phenols, having substituents at one or both of the positions *ortho* to the phenolic hydroxyl group, but without substituents at other positions in the aromatic ring. The characterization was based on the reaction of these phenols with TCNE with the formation of crystalline *p*-(tetracyanoethyl)-phenols and *p*-(tricyanovinyl)-phenols. Some spectral characteristics of the two types of phenols are also discussed.

Recently, it was reported by the present authors that 2,6-dimethylphenol reacted with tetracyanoethylene (TCNE) in acetic acid solution forming 4-tetracyanoethyl-2,6-dimethylphenol³. This compound is an intermediate in the formation of 4-tricyanovinyl-2,6-dimethylphenol which was previously prepared by Sausen *et al.*⁴ from the same starting materials. Further investigations in this laboratory of the reaction between monohydric phenols and TCNE have revealed that, under the conditions described in the experimental section, the formation of crystalline *p*-(tetracyanoethyl)-phenols only took place for certain *ortho* substituted phenols.

Of the tested phenols, no one with a substituent in the position *para* to the phenolic hydroxyl group yielded crystalline derivatives with TCNE. It was hardly to be expected that a reaction should occur with *para* substituted phenols since TCNE, like certain other electrophilic reagents, *e.g.* quinone chloroimides^{5,1}, attacks preferably at the position *para* to the phenolic hydroxyl group⁶.

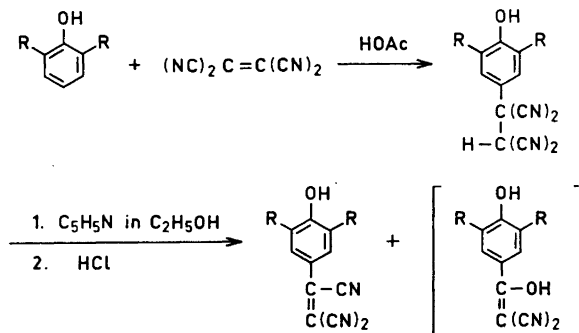
Neither were crystalline tetracyanoethylphenols formed when the *para* position was free and one or both of the *meta* positions occupied. When both of the *meta* positions were filled, the fact that the solution of the components on treatment with pyridine remained colourless proved that no reaction between the phenol and TCNE had taken place (*cf.* Ref.⁶ and the experimental

* Paper No. 7 in a series on analytical investigations of phenols and phenol derivatives. For previous papers, *cf.* Refs. 1,2.

part). When one of the *meta* positions was free a coloured solution resulted in certain cases, *e.g.* for alkylphenols, when the solution of the components was treated with pyridine. This indicated that a reaction between the phenol and TCNE had occurred, although no crystals of the tetracyanoethylphenols were formed. It might be that the yield of tetracyanoethylphenols was too low for any substance to crystallize out from the solution.

While the previously discussed types of phenols did not yield any crystalline derivatives with TCNE, this was the case with certain phenols only substituted in one or both of the *ortho* positions. According to our experience, a slight activation of the phenol by suitable substituents is necessary for the formation of crystalline tetracyanoethylphenols to take place. Thus, when only one substituent is present it should be activating. No crystals for example, were formed with *o*-chlorophenol, although a reaction took place, while *o*-cresol and guaiacol yielded crystalline *p*-tetracyanoethyl derivatives (*cf.* Table 1). When both of the *ortho* positions are occupied, at least one of the substituents should be activating. 2,6-Dichlorophenol, for example, produced no derivative with TCNE whereas 2-chloro-6-methylphenol did. In the case of two substituents in the *ortho* positions, one of the substituents must not be strongly deactivating as indicated by the failure of 2-methyl-6-formylphenol to yield any derivative with TCNE.

The results obtained with some *ortho* substituted phenols have been listed in Tables 1 and 2. The yield of crystals of *p*-(tetracyanoethyl)-phenols was rather varying while the transformation of the latter ones to *p*-(tricyanovinyl)-phenols generally proceeded with good yield. The derivatives were not always easy to obtain in a pure state. There was a tendency for the tetracyanoethylphenols to turn into the tricyanovinylphenols before treatment with pyridine. In the case of *o*-ethylphenol, in fact, no 4-tetracyanoethyl-2-ethylphenol was obtained, but the corresponding tricyanovinyl compound crystallized out on the addition of water. However, sometimes difficulties were encountered in transforming the tetracyanoethyl compound to the tricyanovinyl compound quantitatively. The risk of a continued decomposition of the tricyanovinylphenols must also be taken into account. It has, for example, been shown that 4-tricyanovinyl-2,6-dimethylphenol in alkaline solution is hydrolyzed to



the corresponding α -hydroxy- β,β -dicyanovinyl compound⁴. The formulae above demonstrate the reactions involved in the formation and transformation of (tetracyanoethyl)-phenols.

A feature of the present characterization method is, as was pointed out above, its specificity for *ortho* substituted phenols. These can also be isolated from mixtures with non-reacting phenols using TCNE. 4-Tetracyanoethyl-2,6-dimethylphenol, for example, was obtained in pure state from a mixture of 2,6-dimethylphenol, 3,4-dimethylphenol and *p*-cresol. Before making an attempt to characterize a phenol, using TCNE, it is recommended that the TCNE spot test method, which has been developed in this laboratory, shall be applied (*cf.* Ref.⁶). If this test is negative it is pointless to try to make any TCNE derivatives. If it is positive, a derivative may or may not be formed, depending on the structure.

If there exists any uncertainty about whether the tetracyanoethyl- or tricyanovinylphenol has been formed or about their purity the infrared spectra in the range 2–7 μ should be run. These are, namely, strikingly different for the two types of phenols. In Fig. 1 the spectra of 4-tetracyanoethyl- and 4-tricyanovinyl-2,6-dimethylphenol are shown. These spectra are typical of the two kinds of phenol derivatives.

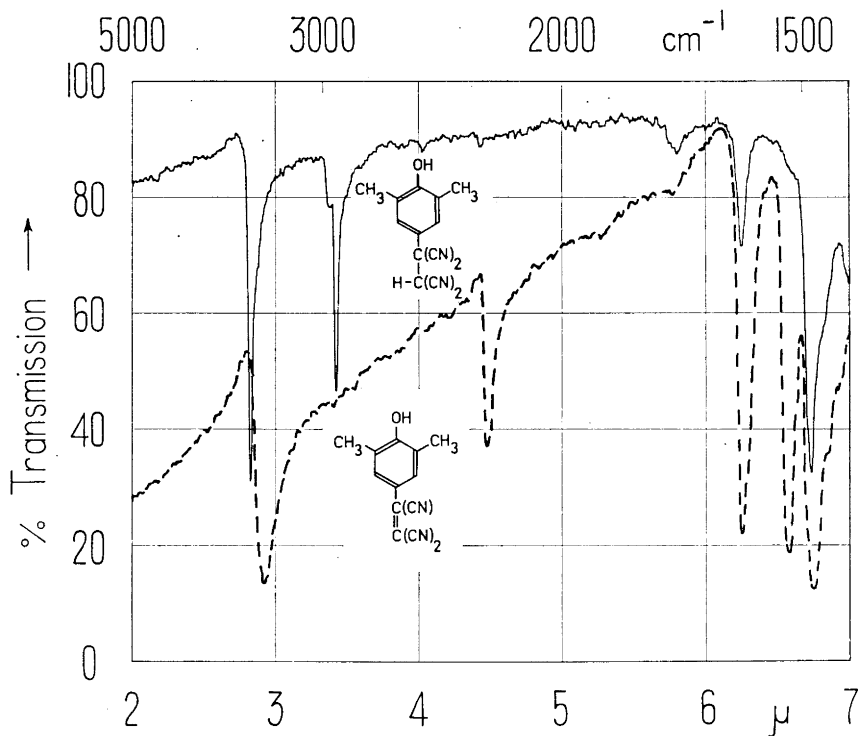


Fig. 1. Infra-red spectra of 4-tetracyanoethyl-2,6-dimethylphenol (—) and 4-tricyanovinyl-2,6-dimethylphenol (---).

The absorption in the hydroxyl stretching region (3μ) of the tetracyanoethylphenols with alkyl and halogen substituents gave rise to a narrow band in the region $3470\text{--}3550 \text{ cm}^{-1}$, except for the 2,6-*ditert.*-butyl compound which absorbed at 3650 cm^{-1} . Since the free-hydroxyl stretching frequency of 2,6-*ditert.*-butyl-4-methylphenol⁷ has been given as 3649 cm^{-1} it appears, that the tetracyanoethylphenol in question is essentially monomeric in the solid state.

Phenolic absorption in the region of 3500 cm^{-1} is considered to be due to hydrogen bonded dimers⁸. On this account, it seems that the other tetracyanoethylphenols with alkyl and halogen substituents to a great extent exist in hydrogen bonded dimeric forms in the solid state. The presence of methoxyl groups shifted the absorption to $3370\text{--}3400 \text{ cm}^{-1}$. At the same time a certain broadening of the bands took place. This shift can be interpreted as an increased association due to the improved possibilities for hydrogen bonding.

Replacement of the tetracyanoethyl group by the tricyanovinyl group shifted the hydroxyl stretching absorption to lower frequencies and made the bands broader. *Diortho* substituted tricyanovinylphenols with alkyl, allyl or halogen in the *ortho* positions absorbed at $3400\text{--}3460 \text{ cm}^{-1}$ and the monoalkyl and methoxyl substituted compounds at $3320\text{--}3335 \text{ cm}^{-1}$. 4-Tricyanovinyl-2,6-*ditert.*-butylphenol provided an exception in yielding a narrow band at 3600 cm^{-1} . The shift to lower frequencies and the broadening of the bands are typical of an increased association. It might be assumed to be due to the greater acidity of the tricyanovinylphenols in comparison with the tetracyanoethylphenols, resulting from the conjugation of the aromatic ring with the tricyanovinyl group.

An examination of the absorption bands in the C—H stretching region at about 3.5μ showed that a well developed band was present in the spectra of the tetracyanoethylphenols while, for the tricyanovinylphenols, in several cases, no indication of any absorption was given. This was undoubtedly partly caused by the fact that the turbidity of most of the potassium bromide disks, obtained for the tricyanovinylphenols, resulted in low light transmission. However, the spectra of methylene chloride solutions* of the tetracyanoethyl- and tricyanovinylphenols also showed a distinct difference in absorption intensity in this region. It might be that the greater absorption of the tetracyanoethylphenols in the C—H stretching region is connected with the presence of a hydrogen atom at the tetracyanoethyl group.

The absorption in the $\text{C}\equiv\text{N}$ stretching region at 4.5μ is of particular interest. In the spectra of the tetracyanoethylphenols no indication was given of the presence of nitrile groups. This fact was somewhat unexpected since in compounds only containing C and H in the neighbourhood of the nitrile group the $\text{C}\equiv\text{N}$ stretching band has generally been found to be strong and also its strength a function of the number of nitrile groups (*cf.* Ref.⁹, p. 225). From an analytical point of view the absence of a nitrile absorption band in the tetracyanoethylphenols is very convenient, because a strong band is given by the tricyanovinylphenols. On this account, the presence of a tricyanovinyl-

* The compounds were not sufficiently soluble in carbon tetrachloride or carbon disulphide. The absorption of the methylene chloride was compensated for.

Table 1. 2- and 2,6-Substituted 4-tetracyanoethyl-phenols.

Substituents	Yield %	M.p. °C	Colour	% N	
				Found	Calc.
CH ₃ —	41	118—119	Light yellow	23.1	23.72
CH ₃ CH ₃	81	144—145*	White	22.2	22.39
CH ₃ <i>n</i> -C ₃ H ₇	38	117—119	White	20.6	20.13
iso-C ₃ H ₇ iso-C ₃ H ₇	80	107—108	Light yellow	18.4	18.29
<i>tert.</i> -C ₄ H ₉ <i>tert.</i> -C ₄ H ₉	81	149—151	White	17.1	16.76
CH ₂ CH=CH ₂ CH ₂ CH=CH ₂	37	92—94	Light yellow	18.5	18.53
CH ₃ Cl	23	145—146	White	19.9	20.70
OCH ₃ —	46	144—146	Light yellow	21.7	22.30
OCH ₃ OCH ₃	46	156—158	White	19.6	19.85

* In a previous communication³ this m.p. was by mistake reported to be 154—156°.

in a tetracyanoethylphenol makes itself known as an absorption at about 4.5 μ. The C≡N stretching frequency of the tricyanovinylphenols, being in the range 2225—2235 cm⁻¹, was in close agreement with the value (2232 cm⁻¹) given by Looney and Downing¹⁰ for the C≡N stretching frequency of tricyanovinylbenzene.

Of value for the differentiation between tetracyanoethyl- and tricyanovinylphenols is also the 6.2—6.9 μ range. The absorption of aromatic compounds in this region is due to C=C stretching vibrations in the aromatic ring and two bands, one near 1600 cm⁻¹ and the other near 1500 cm⁻¹, are characteristic of the benzene ring (*cf.* Ref.⁹, p. 59). In the spectra of all tetracyanoethylphenols with alkyl and halogen substituents, these two bands appear (*cf.* Fig. 1). In the spectra of the corresponding tricyanovinylphenols, a third absorption band at 1517—1537 cm⁻¹ is present between the two other bands.

Table 2. 2- and 2,6-Substituted 4-tricyanovinyl-phenols.

Substituents	Yield %	M.p. °C	Colour	% N	
				Found	Calc.
CH ₃ —	61	137—139	Brown-yellow	19.5	20.09
C ₂ H ₅ —	35	108—109	Orange-yellow	18.2	18.83
CH ₃ CH ₃	95	179—181	Orange-yellow	18.3	18.83
CH ₃ <i>n</i> -C ₃ H ₇	94	151—153	Yellow	17.0	16.72
iso-C ₃ H ₇ iso-C ₃ H ₇	92	167—168	Red	14.8	15.05
<i>tert.</i> -C ₄ H ₉ <i>tert.</i> -C ₄ H ₉	62	204—205	Yellow	14.1	13.67
CH ₂ CH=CH ₂ CH ₂ CH=CH ₂	94	82—84	Brown-yellow	15.4	15.27
CH ₃ Cl	80	174—175	Yellow	17.0	17.24
OCH ₃ —	70	201—203	Red	18.8	18.74
OCH ₃ OCH ₃	90	181—183	Dark-red	16.8	16.46

Since the C=C stretching frequency for tetracyanoethylene¹⁰ has been given as 1527 cm⁻¹ we are inclined to consider that the third band in the spectra of the tricyanovinylphenols is connected with the C=C stretching in the tricyanovinyl group. In the spectra of tetracyanoethyl- and tricyanovinylphenols, containing allyl and methoxyl groups, the situation is more complicated in the actual range due to the appearance of additional strong bands.

EXPERIMENTAL

Tetracyanoethylphenols. Tetracyanoethylene (about 4 mmole) and the phenol, in slight excess, were dissolved in a mixture of 25 ml glacial acetic acid and 4 ml water at room temperature. When the coloured solution had become discoloured, water was added dropwise until a weak turbidity appeared. The turbidity was removed by adding a few drops of glacial acetic acid and the solution was placed in a refrigerator. After some time, white to yellow-white crystals were formed. They were separated by filtration, washed with water and recrystallised from methylene chloride/hexane or ethyl acetate/hexane as described below.

The substance was dissolved in the minimum amount of methylene chloride or ethyl acetate at room temperature. The solution was filtered and hexane was added dropwise until the solution became turbid. The turbidity was removed by a few drops of methylene chloride or ethyl acetate. On cooling in an ice-sodium chloride cold bath, crystals of the tetracyanoethylphenol were formed. They were separated by filtration, washed with hexane and dried and stored in a desiccator. It is recommended not to heat the solution during the recrystallization because of the instability of the tetracyanoethylphenols.

Tricyanovinylphenols. The tetracyanoethylphenol (about 0.5 mmole) was dissolved in 10 ml 96 % ethanol. A few drops of pyridine were added and the solution was heated on a boiling water bath for 15–30 min. The cold solution was acidified using 5 N hydrochloric acid in slight excess. Water was added dropwise until the solution became turbid. The turbidity was removed by adding a few drops of ethanol and the solution set aside in a refrigerator. After some time, coloured crystals were formed. They were separated by filtration, washed with water and recrystallised from glacial acetic acid/water. The substance was dissolved in the minimum amount of glacial acetic acid and filtered. Water was added dropwise until the solution became turbid. Heating on a boiling water bath caused the turbidity to vanish and, on slow cooling, crystals of the tricyanovinylphenol were formed. They were separated by filtration and dried and stored in a desiccator.

Infra-red spectra. The infra-red spectra were obtained using the KBr disk technique (about 1 mg substance/300 mg KBr) and a Perkin-Elmer infra-red spectrophotometer, Model 21.

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