An Unexpected Complex from the Reaction between 2,3-Dichloro-5,6-dicyanobenzoquinone and Amidopyridines

Paolo Bruni,[a] Giorgio Tosi,[a]* and Giovanni Valle[b]

[a] *Dipartimento di Scienza dei Materiali e della Terra, Università degli Studi, Facoltà di Ingegneria, Via Brecce Bianche, I-60131 Ancona, Italy*

[b] *Istituto di Chimica Organica, Università degli Studi, Via Marzolo, 1 - I-35100 Padova, Italy*

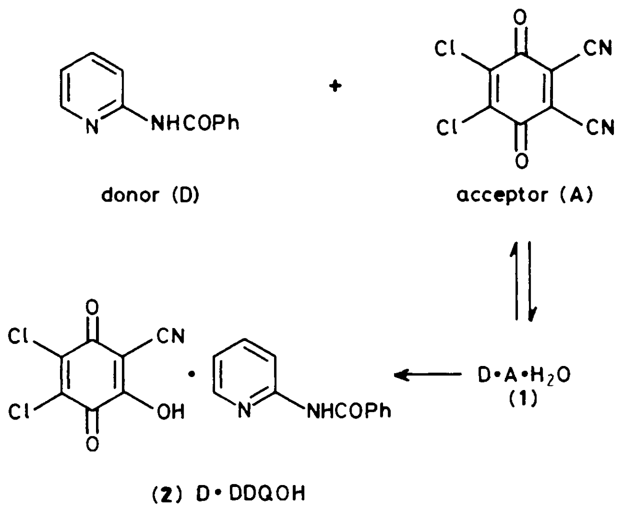
Traces of water induce OH substitution of one of the CN groups in 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), during complexation of DDQ with amidopyridines, while simple hydrolysis of DDQ leads to the corresponding ammonium salt.

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ), which acts as a powerful acceptor in synthetic oxidative processes[1] and in the formation of highly conductive charge transfer complexes,[2] is normally used under rigorously anhydrous conditions. Previously[3] we have described the formation of 1:1 molecular complexes between DDQ and 2-, 3-, 4-aminopyridines in anhydrous media: the complexes were stable in the solid state, but suitable crystals could not be obtained for *X*-ray analysis.

With benzamido- and acetamidopyridines in dichloroethane solution, DDQ forms only 'transient' complexes:[4] in the case of 2-amidopyridines, the presence of traces of water in the solvent causes the formation of a solid donor–acceptor–H_2O (1:1:1) molecular complex (**1**) which, in ethanol (95%) or dichloroethane with traces of water, leads to an unusual new complex (**2**) between the pyridine derivative and the transformed DDQ in which one of the CN ligands is replaced by an OH group (Scheme 1).

The complex was obtained by mixing equimolar amounts of 2-benzamidopyridine and DDQ in dichloroethane solution. After standing for 24 h, red crystals were recovered together with few black crystals of the pyridine–DDQ–H_2O complex (**1**). On boiling the mixture in ethanol or dichloroethane–water, the black crystals disappeared and only pure red crystals, suitable for *X*-ray analysis were obtained.

Substitution of a cyano group by an alkoxy group in DDQ (or similar quinonoid compounds) and by an hydroxy group in 2,3-dicyano-1,4-naphthoquinone (by treatment with sodium



Scheme 1

hydroxide) has been mentioned in the literature,[5—7] but to our knowledge this is the first report of substitution of a cyano group by an hydroxy group in the DDQ molecule. Any attempt to perform this reaction by the Reynolds and Van Allan procedure[6] failed, owing to the rapid decomposition of the reaction product. However, DDQOH is stable when involved in a charge transfer complex. In addition, attempts to synthesize DDQOH from the reaction of DDQ with water, using various solvents and conditions, led to the formation of the $DDQONH_4$ salt, which, when treated with 2-benzamidopyridine, again formed the DDQOH–2-benzamidopyridine complex (**2**).[4]

The geometry of the complex (**2**)† is illustrated in Figure 1. The DDQOH ring planes deviate slightly from planarity (σ = 0.012 Å), with rings adopting a shallow twistboat conformation. The molecular dimensions are in agreement with those found in *o*-benzoquinone[8] and analogous compounds, except the following: the C(3)–C(4) bond (1.537 Å) is longer than the corresponding bond in trigonally hybridized C atoms; the C(4)–C(5) bond (1.379 Å) is longer than a usual double bond; and the C(4)–O(3) bond (1.250 Å) is shorter than usual C–OH distance. In the crystal, the DDQOH molecules form parallel layers, with interlayer separation 3.35 Å (Figure 2). The benzamidopyridine molecule is quasi planar, with normal values for distances and angles. The two parts of the complex are quasi coplanar and are connected by hydrogen bonds between O(3) and N(2), N(3) (2.824 and 2.910 Å, respectively) and between O(1) and N(2), C(8) (2.963 and 3.031 Å, respectively).

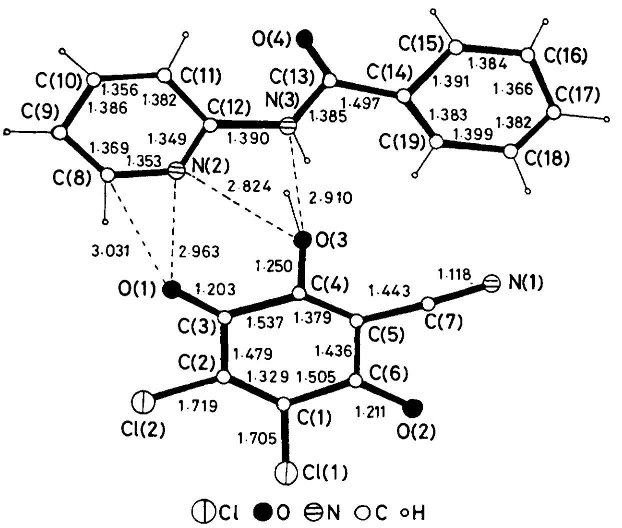


Figure 1. Crystal and molecular structure of 2-benzamidopyridine•DDQOH (**2**) complex as viewed down the *b* axis. The short contacts between the donor and acceptor molecules are indicated by broken lines.

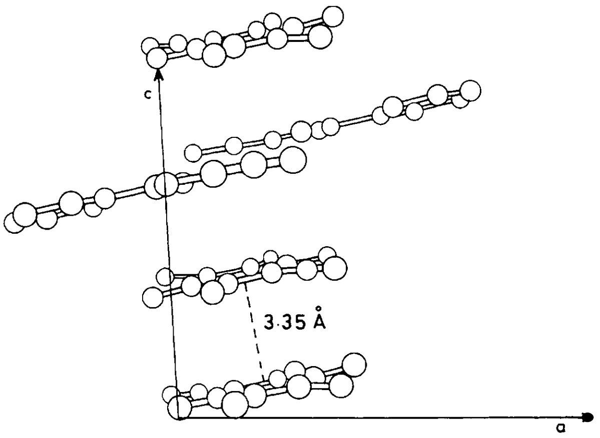


Figure 2. The crystal structure of the 2-benzamidopyridine•DDQOH (**2**) complex as viewed along the crystallographic *b* axis.

Received, 7th March 1988; Com. 8/00905H

References

1 A. J. Fatiadi, 'Preparation and Synthetic Applications of Cyano Compounds,' ed. S. Patai, 'The Chemistry of Triple Bonded Groups,' Suppl. C., Wiley, New York, 1983, 1209.

2 J. J. Mayerle and J. B. Torrance, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3170.

3 G. Tosi, P. Bruni, and L. Cardellini, *Gazz. Chim. Ital.*, 1984, **114**, 125.

4 G. Tosi, P. Bruni, L. Cardellini, P. Stipa, and G. Bocelli, results to be published.

5 H.-D. Becker, *J. Org. Chem.*, 1969, **34**, 1203.

6 G. A. Reynolds and J. A. Van Allan, *J. Org. Chem.*, 1964, **29**, 3591.

7 The formation of a tricyanoethenol derivative is hypothesized in the base-catalysed hydrolisis of tetracyanoethylene to the corresponding pentacyanopropene: W. J. Middleton, E. L. Little, D. D. Coffmann, and Engelhardt, *J. Am. Chem. Soc.*, 1958, **80**, 2795.

8 K. J. Weperen, Van and G. J. Visser, *Acta Crystallogr., B*, 1972, **28**, 338.

---

† The structure of the complex was confirmed by elemental analyses, n.m.r. and mass spectrometry.

Crystal data for (2-benzamidopyridine · DDQOH): $C_{12}H_{10}N_2O$–$C_7HCl_2NO_3$, M = 417.228, triclinic, space group $P\bar{1}$, a = 11.217(2), b = 10.032(2), c = 10.092(2) Å, α = 58.7(2), β = 66.3(2), γ = 68.2(2)°, Z = 2, was treated as triclinic $I\bar{1}$ with a = 11.961(2), b = 14.667(2), c = 10.080(2) Å, α = 88.6(2), β = 93.3(2), γ = 100.6(2)°, Z = 4, D_c = 1.597 g cm^{-3}, Mo-K_α radiation. 1881 Independent observed reflections [$I \geqslant 3\sigma(I)$] were obtained on a Philips PW 1100 diffractometer, θ—2θ scan mode to 2θ = 50°. The structure was phased by Multan 80 program and refined by the least-squares SHELX 76 program to a final R = 0.0624 {$w = 1/[\sigma^2(F) + 0.001\ (F)^2]$}. All non hydrogen atoms were anisotropic and hydrogen atoms were located on a difference map and refined with isotropic U. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.