

## A Ubiquinol-Based Charge-Transfer Complex Obtained from a Solvent-Free Approach

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Quinones (= cyclohexa-2,5-diene-1,4-diones) and hydroquinones (= benzene-1,4-diols) belong to species that are balanced between their redox character and their ability to build supramolecular complexes. Considering the ubiquinol 2,3-dimethoxy-5-methyl-1,4-dihydroquinone (= 2,3-dimethoxy-5-methylbenzene-1,4-diol; **1**), the tendency to undergo an oxidation side reaction was overcome by combining this electron-donating species **1** with a nonreactive partner, benzene-1,2,4,5-tetracarbonitrile (TCNB; **3**), to yield a 2 : 1 charge-transfer (CT) complex **4**. This work illustrates how very convenient the solvent-free techniques are to access intermolecular species. X-Ray diffraction studies revealed that pure ubiquinol **1** (structure included) crystallizes in two enantiomeric conformations, while the triads **4** formed with TCNB (**3**) exist as *meso* forms assembled *via* H-bonds in zigzag-chains patterns.

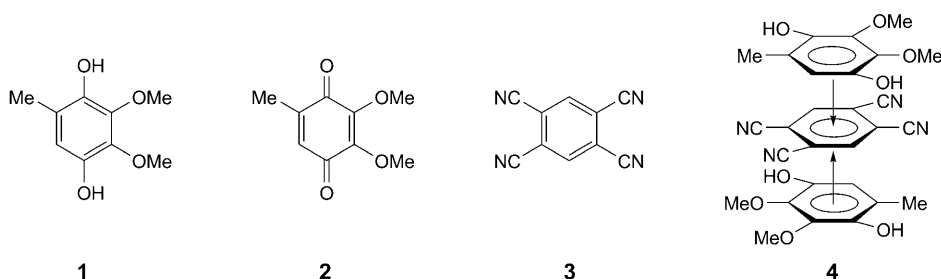
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**1. Introduction.** – Ubiquinones, *i.e.*, 6-isoprenoid-substituted 2,3-dimethoxy-5-methylcyclohexa-2,5-diene-1,4-diones and ubihydroquinones are involved in a wide range of biological processes. Thus, the bacterial reaction centre, which is a membrane-bound bacteriochlorophyll – protein complex responsible for the light-induced electron transfer and associated proton-uptake reactions in bacterial photosynthesis, contains two ubiquinone molecules [1]. Recently, the critical role of a thiolate – ubiquinone charge-transfer (CT) complex in disulfide-bond generation by the inner-membrane protein DsbB, which is present in *Escherichia coli*, has been reported [2]. Other authors proposed a quinhydrone-type complex as being responsible for the absorption properties observed during the disulfide-bond formation [3] (quinhydrone = quinone/hydroquinone 1 : 1 = cyclohexa-2,5-diene-1,4-dione/benzene-1,4-diol 1 : 1). Elsewhere,  $\pi$ -stacking interactions involving phyloquinone a 3-isoprenoid-substituted 2-methylnaphthalene-1,4-dione, *i.e.*, another substituted quinone, were also assumed to take part in the photosystem I activity [4].

The control of self-organization *via* intermolecular interactions is currently of much interest in chemistry, materials science, and biological systems [5–7]. Among CT complexes, quinhydrones are often cited to illustrate how supramolecular complexes can be built up around the subtle balance between noncovalent interactions, such as H-bonding and  $\pi$ – $\pi$  stacking [8–10]. Quinhydrones are commonly described as a tandem of an electron-donating hydroquinone moiety associated through  $\pi$ -stacking interactions to an electron-withdrawing quinone entity. However, less is known about their

exact structure even though they are claimed to exist on the basis of their strong absorption band in the VIS region, signature of an induced CT process. As a matter of fact, only a restricted number of resolved X-ray structures of quinhydrone obtained from substituted quinone or hydroquinone derivatives are available in the literature. Although the acceptor/donor 1:1 stoichiometry is the most commonly encountered, other examples exist with 2:1 [11–13] or 1:2 [14][15] ratios. Furthermore, besides the stacked pattern of these complexes, strong associations *via* H-bonding lead to chains formation [16] or real polar planes [17].

Recently, we reported a convenient approach to a quinone/hydroquinone complex starting from the solid forms under vacuum to overcome the solvation-energy effect involved in the quinhydrone crystallization process [17]. Following the outcomes obtained with 2-methoxy-1,4-quinone/2-methoxy-1,4-hydroquinone, we broadened the range of tested molecules in a systematic way. Thus, we successfully prepared single crystals of a new series of quinhydrone obtained from 1,4-quinones, 2-methoxy-1,4-quinones, and 2,6-dimethyl-1,4-quinones associated with 1,4-dihydroquinones, 2-methoxy-1,4-hydroquinones, and 2,3,5,6-tetrafluoro-1,4-hydroquinones as starting species [18]. Dealing with methoxy derivatives, these stimulating results have prompted us to test the noninnocent ubiquinol 2,3-dimethoxy-6-methyl-1,4-dihydroquinone (CoH<sub>2</sub>Q<sub>0</sub>; **1**), a reduced coenzyme Q without an isoprenoid side chain.



From an experimental point of view, the co-grinding of a solid quinone in a mortar with its corresponding solid hydroquinone proved to be the simplest and most efficient method of obtaining quinhydrone [19]. It also constitutes a preliminary test to readily check the feasibility of the expected match and allows a subsequent UV/VIS analysis in KBr pellets. However, if the two starting components are differently substituted, a redox side reaction can occur that theoretically leads to the formation of four different acceptor/donor pairs. In the case of the ubiquinone 2,3-dimethoxy-5-methyl-1,4-quinone (CoQ<sub>0</sub>; **2**) and ubiquinol **1**, this method does not lead to any characteristic expected colored product. Moreover, the co-grinding of **1** and 2-methoxy-1,4-quinone produced a purple powder that was associated with the symmetrical 2-methoxyquinhydrone [17]. Owing to their substituents, combining mesomeric and inductive effects, ubiquinone **2** and ubiquinol **1** were found to be particularly reactive species. An ubiquinone acts as an oxidizing reagent, while an ubiquinol is rather sensitive to a reoxidation process. It is reasonable to believe that these behaviors provide *in vivo* fast redox reactions through easily switchable species.

To ensure the CT-complex generation, a tuning has to be developed by the subtle substitution of the aromatic rings, thus modulating the acceptor/donor character of the selected quinone/hydroquinone pair. Therefore, the underlying redox activity (URA) plays a key role in such supramolecular assemblies.

By analogy with the situation encountered with a calix[4]arenequinone [20], we finally concluded that neither the co-grinding nor the solvent-free approach would provide any ubiquinhydrone formation in the case of **1** and **2**. This also holds for the 2,6-dimethoxy-1,4-quinone and its hydroquinone from which we have been unable to generate a quinhydrone derivative. As established previously, the underlying redox activity imposes a restricted choice of acceptor–donor pairs. For example, in the case of the pair 2-methoxy-1,4-hydroquinone/1,4-benzoquinone, the obtained quinhydrone resulted from a preliminary redox reaction consisted of the assembly of two molecules of 2-methoxy-1,4-quinone with one molecule of 1,4-hydroquinone [13].

Since, up to now, attempts to apply the above-mentioned solvent-free processes to obtain an ubiquinhydrone from **1** and **2** have failed, we chose to associate ubiquinol **1** to another type of acceptor molecule, namely benzene-1,2,4,5-tetracarbonitrile (TCNB; **3**), which is known for its ability to form CT complexes [21–24]. Among the desirable features compared to quinones, TCNB presents a rather weak volatility and cannot play a role in redox reactions, since this molecule constitutes a relative inert species.

Here, we report the first crystal structure of a CT complex involving an ubiquinol.

**2. Results and Discussion.** – 2.1. *Solvent-Free Reactions.* Interestingly, the co-grinding of solid TCNB (**3**) with  $\text{CoH}_2\text{Q}_0$  (**1**) yielded a beetroot-red powder; its VIS spectrum (KBr) showed the characteristic CT band at 535 nm. Thus, heating **1** and **3** under primary vacuum in a two-separated-compartments home-made sublimator (Fig. 1) [17] led, after 3 h, to the formation of dark red single crystals of **4**. TCNB (**3**) was heated at  $100^\circ$  in the central compartment, whereas ubiquinol **1** was heated at  $45^\circ$  in the side part of the sublimator.

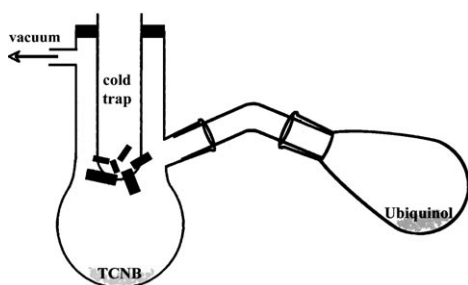


Fig. 1. Home-made sublimator with two separated compartments: production of single crystals of **4** from **1** and **3**

2.2. *Structural Studies. Crystal Structure of  $\text{CoH}_2\text{Q}_0$  (**1**).* Among the ubiquinones,  $\text{CoQ}_0$  (**2**) is the unique representative whose crystal structure is known [25].  $\text{CoH}_2\text{Q}_0$  (**1**), as obtained by sublimation under vacuum, crystallizes in the noncentered monoclinic space group *Cc*. Remarkably, in the X-ray crystal structure of **1** the C-atoms of the MeO groups lie outside the mean plane by 1.385 (C(8)) and 1.165 (C(9)) Å,

providing a chiral entity. In the cell, the two enantiomeric conformations correspond to each other by a translating mirror plane.

For clarification purposes, we considered useful to mention the assignment of the conformations evidenced in the X-ray crystal structure of **1**. The chirality (*R*) or (*S*) is defined by the position of the two MeO groups relative to the aromatic ring; one can consider the rotation direction from bigger to smaller groups, as seen from the MeO group above the aromatic ring (= reference group; *Fig. 2*). Another nomenclature uses the stereodescriptors (*P*) or (*M*) following the helical geometry. Thus, the two enantiomeric conformations of **1** adopt (*M*) or (*P*) configurations, associated to (*S*) or (*R*) configurations, respectively. It should be noticed that the presence of the Me group does not affect the attribution because it belongs to the plane of chirality.

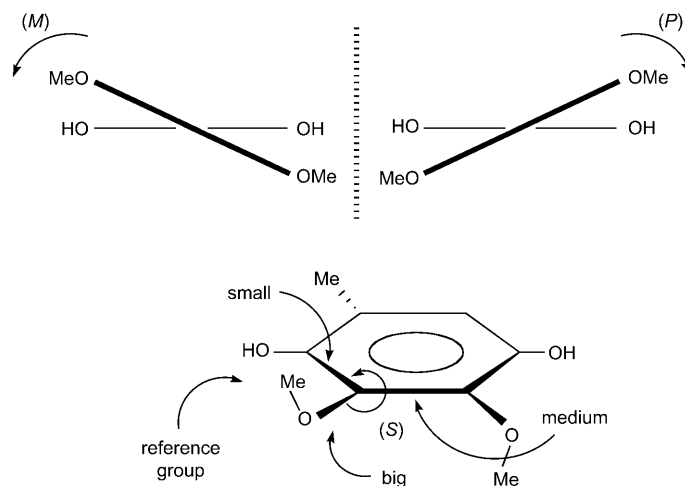


Fig. 2. Assignment of the two enantiomeric conformations of **1**: (*M*) and (*P*) geometries (top) and (*S*) conformation in the (*R*)/(*S*) denomination (bottom)

In pure **1**, no  $\pi$ - $\pi$  interactions occur (angle between mean planes:  $56.07^\circ$ ), and the crystalline arrangement results from strong H-bonds providing a pattern of interlocked molecules,  $O(1) \cdots H(4) = 2.130 \text{ \AA}$ ,  $O(1) \cdots O(4) = 2.996 \text{ \AA}$ , angle  $O(4) \cdots H(4) - O(1) = 165.02^\circ$  and  $O(4) \cdots H(1) = 2.264 \text{ \AA}$ , angle  $O(1) - H(1) \cdots O(4) = 157.52^\circ$  (for atom numbering, see below, *Fig. 3, a*, left). Additionally, short intramolecular distances exist, namely  $O(1) \cdots O(6) = 2.755 \text{ \AA}$ ,  $O(4) \cdots O(5) = 2.793 \text{ \AA}$ , and  $O(5) \cdots O(6) = 2.858 \text{ \AA}$ .

*Crystal Structure of  $(CoH_2Q_0)_2 \cdot TCNB$  (**4**)*. The asymmetric unit of **4** is composed of one molecule of **1** and half a molecule of **3** (*Fig. 3*). As a matter of fact, **4** is a 2 : 1 complex of **1** and **3**, as it is the case in only few examples of quinhydrone. The molecule **3** lies in the center of the unit cell in addition to the eight corner points, but not forming a body-centered lattice since they are not related by translation only. The aromatic moieties of **1** and **3** are tilted by  $14.52^\circ$  as defined by their mean planes. The distance between their centroids is  $4.302 \text{ \AA}$ . The distance from the centroid of unit **3** to the mean planes of units **1** is  $3.20 \text{ \AA}$ , as defined from the projection along the normal to these

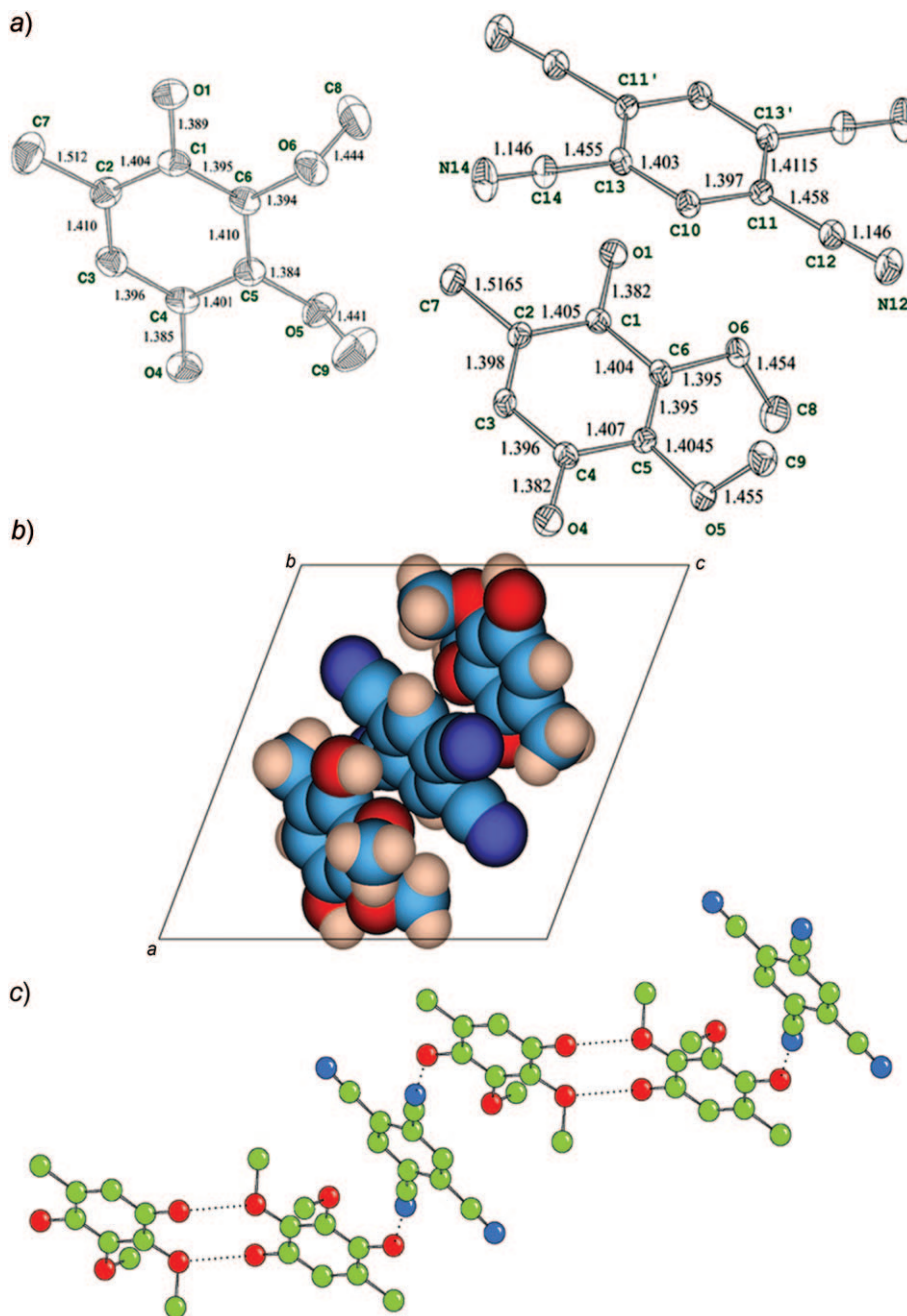


Fig. 3. X-Ray crystal structure: a) ORTEP representations (30% probability level) of the asymmetric units for **1** (left) and **4** (right), resp. (arbitrary atom numbering; bond lengths in Å), b) projection of **4** on the (010) plane: view of a DAD triad (80% van der Waals radii), and c) view of the molecules interacting by H-bonds (dotted lines) showing a chain in the (110) plane (H-atoms are omitted for clarity)

planes, indicating strong  $\pi$ – $\pi$  interactions. So, the structure is composed of donor–acceptor–donor (DAD) triads.

The displacement of a triad allows an O-atom of each ubiquinol unit **1** to lie immediately above the C(10)–C(11) bond, leading to the shortest intermolecular distances between the donor and acceptor units at 3.120 Å (C(11)⋯O(1)) and 3.231 Å (C(10)⋯O(1)). Each unit **1** is connected to its mirror image by an inversion center through two H-bonds (O(4)⋯O(5') = 2.864 Å (= O(5)⋯O(4')) and angle O(4)⋯H(4)–O(5') = 142.71°), and also to a unit **3** via an H-bond that involves an N-atom (O(1)⋯N(14) = 2.981 Å, angle O(1)–H(1)⋯N(14) = 153.53°) (Fig. 3). This provides a zigzag chain orientation in the (110) plane with a periodicity of 20.565 Å, as determined from the distance between the centroids of two consecutive TCNB (**3**) molecules.

The chains are connected to each other through  $\pi$ – $\pi$  interactions, defining sheets parallel to the (110) plane. Chains including units **3** at the center of the cell make an angle of 82° with chains incorporating units **1** in the knots. Therefore, the structure can be described as layers parallel to the (110) plane, with an alternated orientation of the chains from one layer to the next. It is noteworthy that, contrarily to quinhydrone examples, the molecules do not arrange in infinite columns. Additionally, the ArH bond (C(3)–H(31)) of **1** is oriented towards the center of the aromatic ring of units **1** belonging to a neighboring layer, with H(31)⋯centroid (C(1)C(2)C(3)C(4)C(5)C(6)) = 2.79 Å (the distance from this atom to the mean plane is 2.756 Å). Whereas, the units **1** make an angle of 69.59° between their mean planes, these interactions contribute to the interlayer cohesion.

As in compound **1**, the two MeO groups adopt a helical pattern in both sides of the aromatic ring, with the corresponding C-atoms 1.116 (C(8)) and 1.159 (C(9)) Å outside the mean plane, providing a chiral entity. In the structure, the two enantiomers of **1** correspond to each other in each DAD triad by an inversion center.

Since the molecules **1** are not symmetrically substituted, their involvement in a stack conformation leads to a discrimination between the two face orientations and provides de facto chiral species. This situation remains strictly similar to that encountered with ferrocene derivatives tetrasubstituted by two different groups, with each of these groups positioned correspondingly at each cyclopentadienyl moiety [26]. In these compounds, if the two cyclopentadienyl moieties are identically functionalized, a *meso* form exists when an inversion center is located at the Fe-atom.

**2.3. Spectroscopic Studies. Infrared Spectroscopy.** The IR spectrum of complex **4** corresponds to a superimposition of the spectra of **1** and **3**, except for the OH and C≡N vibrations. Complex **4** exhibits two C≡N vibrations at 2247 and 2257 cm<sup>-1</sup>, whereas the starting TCNB (**3**) shows only one C≡N vibration at 2247 cm<sup>-1</sup>. This is in accordance with the existence of H-bonds in **4** that involve only two of the four C≡N moieties, as shown in the crystal structure. The two apparently degenerate modes (b<sub>2u</sub> and b<sub>3u</sub>) in the D<sub>2h</sub> initial space group [27] become discriminated in the C<sub>2h</sub> space group (Fig. 4). Both vibrations are b<sub>u</sub> modes, but correspond to elongations towards the H-bonds direction and along the direction of C≡N groups not involved in H-bonds, respectively. The OH vibration of **4** appears at 3456 cm<sup>-1</sup>, vs. 3423 cm<sup>-1</sup> for pure **1**. In addition, this band is very sharp compared to that of pure **1**, the full width at half maximum (FWHM) being 25 cm<sup>-1</sup> vs. 100 cm<sup>-1</sup>, indicating that all the H-bonds are of the same strength in **4**, in contrast to what occurs in **1**.

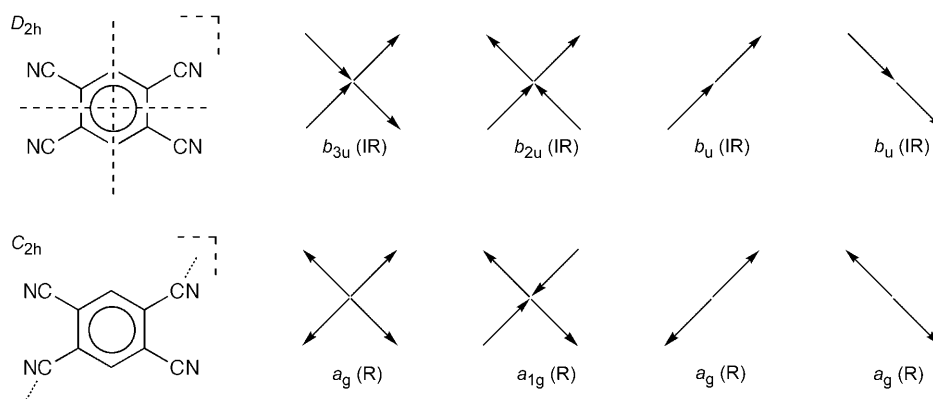


Fig. 4. Schematic view of active vibration modes for the cyano groups of TCNB in infrared (IR) and Raman (R) spectroscopies, in  $D_{2h}$  and  $C_{2h}$  space groups. The mirror planes are shown for the two symmetries as well as the H-bonds for the  $C_{2h}$  symmetry.

**Raman Spectroscopy.** In contrast to the IR spectrum, the *Raman* spectrum of TCNB (**3**) shows two peaks for nitrile vibrations at 2239 and 2249  $\text{cm}^{-1}$ , attributed to  $a_g$  and  $b_{1g}$  modes. These modes lead to two  $a_g$  modes in  $C_{2h}$  symmetry (Fig. 4). However, the *Raman* spectrum of **4** exhibits an additional peak at 2255  $\text{cm}^{-1}$ , showing that the local symmetry is lower than that deduced from X-ray studies, due to the existence of strong  $\pi-\pi$  interactions.

**UV/VIS Spectroscopy.** Whereas the starting materials are white compounds, the UV/VIS spectrum of **4** exhibits a strong and broad absorption band centered at 535 nm (crystals diluted in KBr). Besides, co-grinding of solid **1** and **3** leads to a reddish powder that exhibits the same UV/VIS and IR spectra as **4**. This suggests a solid-state reactivity similar to that encountered with quinone/hydroquinone pairs [13][17]. CT Complex **4** does not exist in solution. Consequently, the  $^1\text{H-NMR}$  spectrum of **4** in  $\text{CD}_3\text{CN}$  remains as a simple superimposition of the spectra of **1** and **3**.

**Theoretical Calculations (MOPAC/MNDO).** To appreciate the effect of the charge transfer, the dipole moments of **1** as a pure compound and as present in **4** were calculated by Chem3D Pro<sup>TM</sup> software with the MNDO [28] method and the geometrical data collected from the single-crystal X-ray structures of **1** and **4** without geometrical optimization. In **1**, the dipole moment, oriented parallel to the C(1)–O(6) direction, is 1.5 D, compared to 1.1 for the optimized geometry. In **4**, it is 2.0 D, also oriented quasi perpendicularly to the OH–OH axis, towards the C(1)–O(6) direction. Thus, the calculated dipole moment for the ubiquinol **1** turns out to be higher in the CT complex than in the pure compound in which molecules are not involved in strong intermolecular interactions.

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## Experimental Part

*2,3-Dimethoxy-5-methylbenzene-1,4-diol (1)*. Diol **1** was synthesized from **2** by reduction with NaBH<sub>4</sub> in EtOH under Ar. Crystals of **1** were obtained by sublimation under primary vacuum.

*Crystal Data of 1*<sup>1)</sup>: C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>, *M<sub>r</sub>* = 184.19, colorless parallelepiped (0.09 × 0.12 × 0.16 mm), monoclinic, *Cc*; *a* = 13.0399(15), *b* = 8.1531(10), *c* = 8.8900(9) Å, β = 96.652(10)°; *V* = 938.78(19) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.30 g cm<sup>-3</sup>. *KappaCCD-Enraf-Nonius* diffractometer, λ (MoK<sub>α</sub>) 0.71073 Å, μ (MoK<sub>α</sub>) = 1.14 cm<sup>-1</sup>; 5059 reflections (*T* 250 K, 3 < θ < 29°); number of independent data collected 1364, number of independent data used for refinement 1143 ((*F<sub>o</sub>*)<sup>2</sup> > 1.5σ(*F<sub>o</sub>*)<sup>2</sup>); merging *R* = 0.0336, *R* = Σ||*F<sub>o</sub>*| - |*F<sub>c</sub>*|| / Σ|*F<sub>o</sub>*| = 0.0352, *R<sub>w</sub>*\* = [Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*||)<sup>2</sup> / Σw*F<sub>o</sub>*<sup>2</sup>]<sup>1/2</sup> = 0.0419; -0.15 < Δρ < 0.26 e · Å<sup>-3</sup>.

*Benzene-1,2,4,5-tetracarbonitrile Compound with 2,3-Dimethoxy-5-methylbenzene-1,2-diol (1:2) (4)*. Crystals of **4** were synthesized from **1** (50 mg, 0.27 mmol) and **3** (50 mg, 0.28 mmol) which were placed in two separated compartments of a home-made sublimator (*Fig. 1*) and both heated gradually up to 45° and 100°, resp. The vacuum (10<sup>-1</sup> Torr) was continuously maintained, and the cold trap filled with water. IR (attenuated total reflection (ATR); main peaks): 3455 (OH); 3109, 3043 (CH, TCNB); 2989, 2947, 2848 (CH, CoH<sub>2</sub>O<sub>0</sub>); 2257, 2247 (CN); 1493, 1475, 1190, 1178, 1113, 1064, 991, 946. *Raman* (785 nm beam of a laser diode in a micro*Raman* set-up on a single crystal; main peaks): 2255, 2249, 2239 (CN); 1605, 1595, 1540, 1257, 1249, 719, 562, 407, 225, 145. UV/VIS (KBr): 535 nm. <sup>1</sup>H-NMR (300 MHz, crystals dissolved in CD<sub>3</sub>CN; δ in ppm, *J* in Hz): 2.10 (*d*, *J*(arom. H, Me) = 0.9, Me); 3.82 (*s*, MeO); 3.85 (*s*, MeO); 6.16 (*br. s*, 2 OH); 6.40 (*q*, *J*(arom. H, Me) = 0.9, 1 arom. H (**1**)); 8.5 (*s*, 1 arom. H (**3**)).

*Crystal Data for 4*<sup>1)</sup>: C<sub>28</sub>H<sub>26</sub>N<sub>4</sub>O<sub>8</sub>, *M<sub>r</sub>* 546.54; burgundy-red parallelepiped (0.08 × 0.11 × 0.15 mm), monoclinic, *P21/n*, *a* = 13.9986(13), *b* = 7.5329(9), *c* = 14.2498(19) Å; β = 112.043(7); *V* = 1392.8(3) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.30 g cm<sup>-3</sup>; *KappaCCD-Enraf-Nonius* diffractometer, λ (MoK<sub>α</sub>) 0.71073 Å, μ (MoK<sub>α</sub>) = 1.14 cm<sup>-1</sup>; 15165 reflections (*T* 250 K, 1 < θ < 30°); number of independent data collected 4052, number of independent data used for refinement 1697 ((*F<sub>o</sub>*)<sup>2</sup> > 1.5σ(*F<sub>o</sub>*)<sup>2</sup>); merging *R* = 0.0692, *R* = Σ||*F<sub>o</sub>*| - |*F<sub>c</sub>*|| / Σ|*F<sub>o</sub>*| = 0.0485, *R<sub>w</sub>*\* = [Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*||)<sup>2</sup> / Σw*F<sub>o</sub>*<sup>2</sup>]<sup>1/2</sup> = 0.0413; -0.31 < Δρ < 0.23 e · Å<sup>-3</sup>.

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<sup>1)</sup> The crystallographic data of **1** and **4** have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-643164 and 643163, resp. Copies of the data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).



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