A quinhydrone-type 2 : 1 acceptor–donor charge transfer complex obtained *via* a solvent-free reaction†

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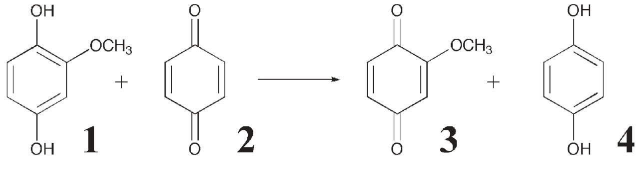
A 2 : 1 2-methoxybenzoquinone (BQ_{OMe})–hydroquinone (H_2Q) complex (5), obtained as single crystals by a solvent-free reaction, combines dipolar and π–π interactions, as well as hydrogen bonding.

Non-covalent interactions, namely hydrogen bonding, halogen bonding, π–π and dipole–dipole interactions stabilize numerous organic, organometallic and biological molecular networks.[1–6] Considering the example of quinhydrone, a well-known charge transfer complex between benzoquinone (BQ) and H_2Q, π–π interactions exist inside the donor–acceptor stacks, whilst infinite molecular chains form through hydrogen bonds between neighboring stacks.[7,8] Elsewhere, charge transfer complexes of the quinhydrone-type have been involved in recognition processes[9] and recently used to self-organize calixarenes.[10] In unsymmetrically-substituted quinhydrones, interconversion by hydrogen transfer was shown to occur between the two components of the complex in the solid state,[11–13] but only one crystal structure was reported.[12] Concerning the association of BQ_{OMe} and H_2Q, a charge transfer band has been observed, but without any information about the stoichiometry of the interaction.[14]

In this paper we describe a new synthetic route to obtain single crystals of quinhydrones through a solvent-free reaction. The starting materials, 2-methoxyhydroquinone H_2Q_{OMe} (**1**) and BQ (**2**), undergo a redox reaction to lead to BQ_{OMe} (**3**) and H_2Q (**4**) (Scheme 1), which evolve to give **5**‡ as black needles (space group: P-1).§ The asymmetric unit is composed of one molecule of **3** and half a molecule of **4** (Fig. 1). Hydroquinone lies at an inversion center, so compound **5** has to be considered as a 2 : 1 acceptor–donor (AAD) complex. The molecules arrange in columns of repeating AAD sequences parallel to the $\left(\vec{c}-\vec{b}\right)$ vector, and make an angle of 30° to this axis. The distance between the molecular planes of the A and D components in a column varies between 3.09 and 3.17 Å (mean value: 3.13 Å), which indicates a strong π–π interaction (Fig. 1). This A–D π-stacking distance is comparable to that observed in the unsubstituted quinhydrone (3.2 Å).[8] We note however that A and D are tilted by 2°. Further, the distance between two neighboring A moieties (3.35 Å) is typical of a π–π interaction, comparable to the intermolecular distance observed in pure **3**.[15] The AA pairs, in which each molecule corresponds to its twin by an inversion center, are stabilized by a dipole–dipole interaction. The dipole moment of **3** has been calculated to be 0.81 Debye (MNDO).[15] Hydrogen bonds exist between H_2Q and BQ_{OMe} molecules belonging to adjacent columns, defining planes parallel to the (011) plane; $d_{O3–O4'}$ = 2.717(2) Å, angle O3–H1′–O4′ = 164° (Fig. 1). These hydrogen bonds involve the carbonyl group in the *meta* position with respect to the methoxy group. The interatomic distances of sub-units **3** in **5** are slightly different from those measured in single crystals of free **3** (space group $P2_1/c$).[15] Due to the existence of hydrogen bonding involving O3, the difference between the two carbonyl distances (C4–O3 − C1–O1) suffers from a slight increase from 0.005(5) to 0.027(5) Å, while the C–OH distance is not significantly shortened, compared to pure **4**.



Scheme 1

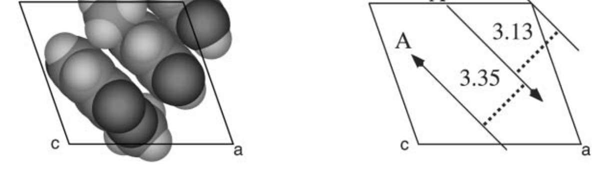


Fig. 1 X-Ray crystal structure of **5**: (a) ORTEP (30% probability level) representation of the asymmetric unit, including atomic numbering and bond lengths in Å; the prime (′) symbol indicates that these atoms are at equivalent positions (1 − x, 2 − y, −z). (b) View of an AAD triad (100% van der Waals radii). (c) A schematic view of the structure with interplanar distances in Å (projection on the (011) plane, segments indicate the main axis of molecules and arrows the direction of the dipolar moment of A).

For sub-unit **4**, we compared data measured in **5** with the mean value obtained from the three independent molecules constituting

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† Electronic Supplementary Information (ESI) available: Optical absorption spectra of a thin film of **1** in PMMA exposed to **2**, (a) as a function of time and (b) difference from the starting film showing the charge transfer band. See DOI: 10.1039/b600345a

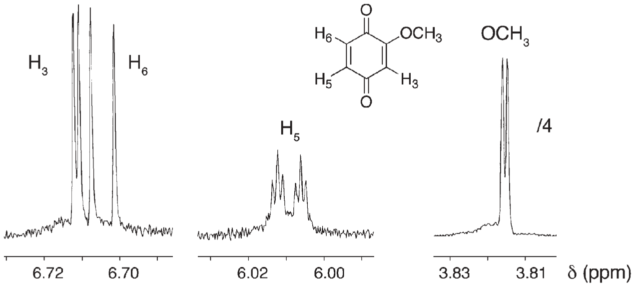

Fig. 2 NMR spectra of **3** in CD_3CN.

the asymmetric unit in **4**, obtained as single crystals by sublimation under vacuum (α-form).¶ The C–C distances measured in **5** are 0.007(4) Å longer than those measured in free **4** (mean values of all the C–C bonds). In spite of the marginal significance of this value, one can note that the difference is 0.014 Å when going from **4** to the BQ/H_2Q quinhydrone, both determined at RT.[8,16]

The ^1H NMR spectrum of an equimolar mixture of **1** and **2** in CD_3CN indicates that the reaction depicted in Scheme 1 is quantitative after a few minutes. The spectrum of crystals of **5** dissolved in CD_3CN confirms that **3** and **4** are in a ratio of 2 : 1. The peaks attributable to **3** were identified from their different coupling constants and homogeneous decoupling experiments. In contrast with previously published works, the signal at δ 6.71 is not a singlet,[17,18] but remains as two doublets (Fig. 2). The methoxy group does not appear as a singlet, but as a doublet. Irradiation at δ 3.8 induces a modification of the peak at δ 6.0, which then appears as a doublet of doublets, without any modification of the other signals. Reversibly, irradiation at δ 6.0 transforms the signal at δ 3.8 into a singlet. This means a coupling phenomenon exists between protons of the methoxy group and H5, which could also be observed in pure $CDCl_3$ and when the solution was diluted ten times in CD_3CN. No variation of chemical shift was observed between pure **3**|| and mixtures of **3** and **4** in CD_3CN, indicating no intermolecular interaction between the acceptor and donor components in that solvent.

In acetonitrile, reaction occurs rapidly between **1** and **2** at room temperature, but the absorption spectra of equimolar mixtures of **1** and **2** correspond to the superimposition of the individual spectra of **3** and **4** (Fig. 3), indicating that products **3** and **4** do not interact.

The absorption spectrum of **5**, obtained in the solid state from a KBr pellet, shows a strong and broad absorption band centered at 575 nm (Fig. 3). Films are violet in color. Solid mixtures of **1** and **2**, and of **3** and **4** show the same spectra as **5**, indicating that the redox reaction occurs rapidly (in the range of minutes) at room temperature.

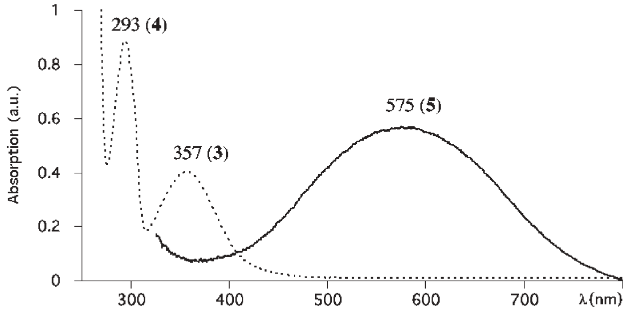

Fig. 3 Absorption spectrum of an equimolar mixture of **1** and **2** in acetonitrile (dotted line), and in the solid state (KBr pellet) (solid line).

We also prepared films from acetonitrile solutions of **1** and poly(methyl metacrylate) (PMMA), which after exposure to **2** at RT exhibited the same charge transfer band. We are now applying the same synthetic route to other more elaborate molecules.

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Notes and references

‡ *Synthesis of compound* **5**: A Schlenk tube containing a mixture of **1** (50 mg, 0.35 mmol) and **2** (50 mg, 0.46 mmol) was purged under argon, evacuated under a primary vacuum and then closed. The tube was heated in a home made vertical oven from room temperature to 100 °C at a heating rate of 0.1° min^{-1}, then maintained at 100 °C for 13 h. 2 cm long black needles were formed 2 cm above the oven. **5**: m.p.: 136 °C (dec.); IR (KBr): 1677 and 1640 (s) (C=O) cm^{-1}; UV-vis: λ_{max} (KBr) 575 nm; ^1H NMR of dissolved crystals (300 MHz, CD_3CN): $\delta = 3.81$ (d, $J_{OCH_3-5} = 0.4$ Hz, 3 H, OCH_3), 6.01 (ddq, $J_{5-6} = 1.9$ Hz, $J_{5-3} = 0.4$ Hz, $J_{5-OCH_3} = 0.4$ Hz, 2 H, H_5), 6.46 (br s, 2 H, OH), 6.70 (s, 4 H, ArH), 6.705 (d, $J_{5-6} = 1.9$ Hz, 2 H, H_6) and 6.71 (d, $J_{3-5} = 0.4$ Hz, 2 H, H_3); ^{13}C NMR (75.47 MHz, CD_3CN): $\delta = 57.2$ (OCH_3), 108.7 (C3), 116.9 (CH, H2Q), 135.7 and 138.0 (C5 and C6), 151.1 (COH, H_2Q), 160.1 (C2), and 183.0 and 189.0 (C1 and C4). Anal. calc. for $C_{20}H_{18}O_8$: C, 62.18; H, 4.70. Found: C, 61.54; H, 4.92%.

§ *Crystal data* for **5**: $C_{20}H_{18}O_8$, $M = 386.36$, triclinic, P-1, $a = 6.6793$ (14), $b = 8.117$ (2), $c = 9.238$ (2) Å, $\alpha = 69.157$ (14), $\beta = 69.931$ (19), $\gamma = 81.34$ (2)°, $V = 439.42$ (19) $Å^3$, $Z = 1$, $D_c = 1.46$ g cm^{-3}. Measured on a KAPPACCD-Enraf Nonius diffractometer: $\lambda(Mo\text{-}K_\alpha) = 0.71073$ Å, $\mu(Mo\text{-}K_\alpha) = 1.14$ cm^{-1}, 8218 reflections ($T = 200$ K, $2 < \theta < 32°$). Number of independent data collected: 2825; number of independent data used for refinement: 1387 $(F_o)^2 > 1.5\ \sigma(F_o)^2$, merging $R = 0.034$, $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o = 0.0578$, $Rw^* = [\Sigma w(\| F_o | - | F_c \|)^2 / \Sigma w F_o^2]^{1/2} = 0.0597$, $-0.297 < \Delta\rho < 0.424$. CCDC 294809. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600345a

¶ *Crystal data* for **4** at 200 K: R-3, $a = b = 38.567$, $c = 5.6650$ Å (α-form, lit.[16] at 300 K, $a = b = 38.46$, $c = 5.650$ Å), $\alpha = \beta = 90$, $\gamma = 120°$, and $Z = 18$.

|| Compound **3** was synthesized from **1** (130 mg, 0.93 mmol) and **2** (100 mg, 0.92 mmol) in CH_3CN and purified on silica gel (eluent: CH_2Cl_2). Yield = 70%. **3**: m.p.: 136 °C (dec.) (lit.[15] 134 °C); IR (KBr): 1679 (s) and 1647 (s) (C=O) cm^{-1}; UV-vis: λ_{max} (CH_3CN) 252 nm (log $\varepsilon = 4.0$) and 357 nm (log $\varepsilon = 3.2$); ^1H NMR (300 MHz, CD_3CN): $\delta = 3.81$ (d, $J_{OCH_3-5} = 0.4$ Hz, 3 H, OCH_3), 6.01 (ddq, $J_{5-6} = 1.9$ Hz, $J_{5-3} = 0.4$ Hz, $J_{5-OCH_3} = 0.4$ Hz, 1 H, H_5), 6.705 (d, $J_{5-6} = 1.9$ Hz, 1 H, H_6) and 6.71 (d, $J_{3-5} = 0.4$ Hz, 1 H, H_3).

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