The Crystal Structure of 2-Methoxy-1,4-benzoquinone: Molecular Recognition involving Intermolecular Dipole–Dipole- and C–H···O Hydrogen Bond Interactions

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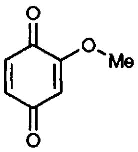
In its crystal structure 2-methoxy-1,4-benzoquinone 2 is networked into a planar hexagonal pattern by intermolecular dipole–dipole- and extensive C–H···O hydrogen bond interactions leading to a graphite-like layer packing motif.

Strong (O–H···O and N—H···O hydrogen bonds)[1,2] and weak (van der Waals, π···π stacking)[3] intermolecular interactions are principal forces for molecular recognition and self-organization of molecules. However, the potential of weak C–H···Y (Y=O, N) hydrogen bonds has been recognized and implicated only recently in the self organization of molecular complexes and aggregates.[4]

Here, we report the crystal structure of 2-methoxy-1,4-benzoquinone **2**,† which possesses a graphite-like layer packing motif hitherto unknown for simple 1,4-benzoquinones;[5] both intermolecular dipole–dipole- and C–H···O hydrogen bond interactions play a decisive role.

The crystal structure of **2** has the space group symmetry $P2_1/c$ with four pairs of two crystallographically independent molecules of **2** [residue 1 (n = 1) and 2 (n = 2)] occupying the unit cell.‡ In Fig. 1, an ORTEP representation of both residues is shown in combination with experimental and theoretical (MNDO[7] [MOPAC 6.0];[8] ΔH_f^0 **2** −72.81 kcal mol^{-1})§ bond lengths. The data reveal that the planar 1,4-benzoquinone skeleton of **2** possesses a merocyanine-type distortion, *i.e.* bond equalization along the 6π-electron/5 centre subunit perimeter [O(n3)C(n4)C(n3)C(n2)O(2)] [n = 1 and 2, respectively] is discernible. Note that the MNDO bond lengths agree satisfactorily with related, averaged bond lengths found in residues 1 and 2. In line with similar structural distortions found in 2,5-electron donor-substituted 1,4-benzoquinones,[5,9] the carbon–carbon bond lengths adjacent to carbonyl group C(n1)O(n1) [n = 1 and 2, respectively] differ in length by 0.027(1) Å (n = 1) and 0.047(1) Å (n = 2) (MNDO 0.025 Å). The elongation of carbon–carbon bond C(n1)C(n2) with respect to C(n1)C(n6) can be rationalized by the asymmetric charge distribution in **2**; the positive total atomic charges [q(MNDO)] found for carbon atoms C(n1) and C(n2) will lead to a reduction of electron density along C(n1)C(n2) [Fig. 1; q(MNDO), C(n1) 0.2804, C(n2) 0.1164 and C(n6) −0.1011].[10] Using similar arguments, the differ-



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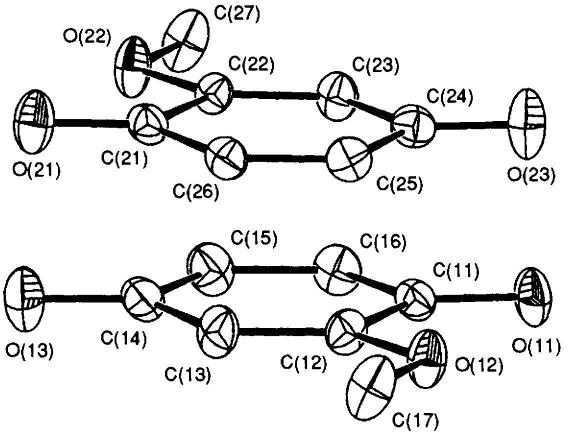

Fig. 1 ORTEP (50% probability level) representation of the two independent molecules of **2**; residues 1 and 2 are related by a non-crystallographic inversion centre. Residues 1 and 2 are stacked in the c-direction. Bond lengths in Å for **2** (n = 1, n = 2) and MNDO values in square brackets) and MNDO total atomic charges in q: O(n1)C(n1); 1.219(4), 1.217(4) [1.223], C(n1)C(n6); 1.467(4), 1.467(4) [1.502], C(n5)C(n6); 1.327(5), 1.323(5) [1.348], C(n4)C(n5); 1.468(6), 1.481(5) [1.498], O(n3)C(n4); 1.228(5), 1.219(5) [1.228], C(n3)C(n4); 1.451(5), 1.454(4) [1.490], C(n2)C(n3); 1.341(5), 1.331(5) [1.367], C(n1)C(n2); 1.494(5), 1.514(5) [1.527], O(n2)C(n2); 1.336(4), 1.338(4) [1.350], O(n2)C(n7); 1.444(5), 1.447(5) [1.405] and O(n1); −0.2330, C(n1); 0.2804, C(n2); 0.1164, C(n3); −0.2248, C(n4); 0.2891, O(n3); −0.2759, C(n5); −0.0772, C(n6); −0.1011, O(n2); −0.2617, C(n7); 0.2081.

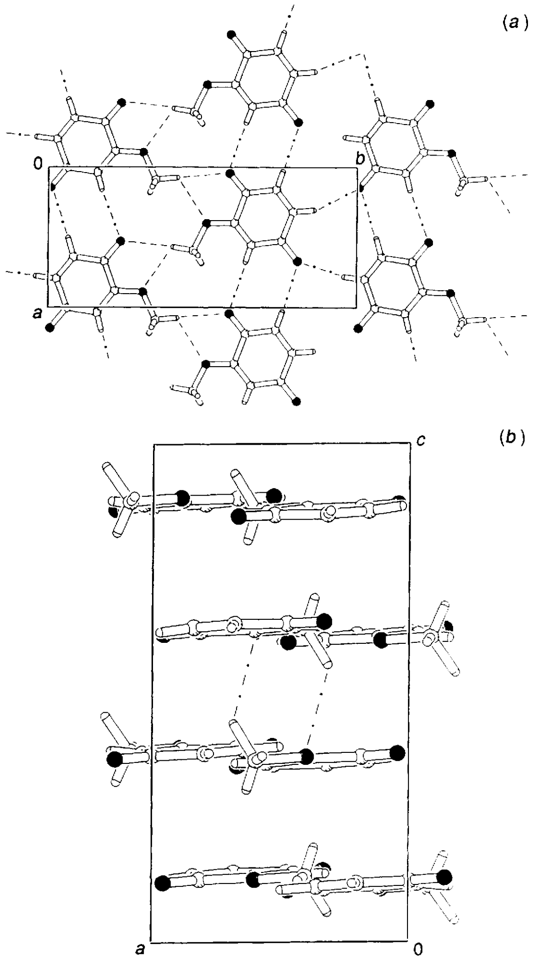

Fig. 2 Sheet structure of **2** parallel to ab-plane (a) and its stacking pattern in the c-direction (b) [C–H···O hydrogen bonds are represented by ---- (linear) and --- (bifurcated)]‡

ence between the carbon–carbon bond lengths adjacent to carbonyl group C(n4)O(n3) [n = 1 and 2, respectively] will be less pronounced {Fig. 1; 0.017(1) Å (n = 1), 0.027(1) Å (n =2) and MNDO 0.008 Å [q(MNDO); C(n4) 0.2891, C(n3) −0.2248 and C(n5) −0.0722]}. Consequently, compound **2** possesses a dipole moment [μ(MNDO)=0.81 D§] which will affect its solid-state packing motif (see below).¶

The crystal structure of **2** consists of planar sheets parallel to the *ab*-plane with all atoms, except for two of the methyl hydrogen atoms, positioned within standard deviation in the best plane [Fig. 2(*a*)]. The two crystallograpically distinct molecules of **2** crystallise in alternating infinite ribbons of residues 1 and 2 which are related by a non-crystallographic glide-plane. Alternatively, the crystal structure of **2** can also be envisaged to consist of 'dimers' of one residue 1 and one residue 2 in the *c*-direction which are related by a non-crystallographic inversion centre (Fig. 1; centre-to-centre distance 3.64 Å, angle between the centre-to-centre vector and the normals of both residues 23.7°). Apparently in this way, unfavourable intermolecular dipole–dipole interactions both in the *ab*-plane and in the *c*-direction are minimized. Since the angle between the normal of the best plane of residue 1 and 2, respectively, in the *c*-direction is only 0.19(9)°, the sheets run parallel with an intersheet distance of 3.3 Å. Hence, they pack efficiently for optimal π···π interactions in a ring over bond motif (Fig. 1 and 2).‡ Remarkably, the occurrence of extensive C–H···O hydrogen bond formation in the sheets is implicated by the observed intermolecular H···O distances and their directionality. According to common hydrogen bond classification criteria,[11] they can be designated as either linear or bifurcated with the carbonyl- or methoxy-oxygen atoms of other molecules **2** acting as acceptor [Fig. 2(*a*)]. With the exception of two H···O distances of 2.63 and 2.61 Å which fall in the range of the sum of van der Waals radii minus 0.05 Å, all H···O distances are smaller than the sum of van der Waals radii minus 0.12 Å (H···O; range 2.38–2.59 Å)! Within and among the ribbons the hydrogen atoms of the 1,4-benzoquinone skeleton form linear C–H···O hydrogen bonds with carbonyl groups. Relevant C–H···O angles are in the range of 157–176° and do not deviate much from linearity [Fig. 2(*a*)].[11] Furthermore, bifurcated C–H···O hydrogen bonds are identified between the in-plane hydrogen atom of the methyl group of residues 1 and 2 with both the carbonyl and methoxy oxygen atom of residues located in the next nearest ribbon. For these weak hydrogen bonds, the sum of valence angles about hydrogen is 344° [residue 1] and 351° [residue 2], respectively, which is in satisfactory agreement with the anticipated value of 360°.[11] In addition, a distorted linear weak C–H···O hydrogen bond with H···O 2.47 Å and a C–H···O angle of 131° is identified between an out-of-plane hydrogen atom of the methyl group of residue 2 and the ether oxygen atom O(22) of a similar residue positioned in the next sheet [Fig. 2(*b*)]. Consequently, the overall effect is that molecules of **2** are efficiently linked by an intricate interplay of merocyanine-type and weak C–H···O hydrogen bond interactions into planar hexagonal networks which stack in the *c*-direction leading to a structural motif reminiscent of graphite (**2**; packing coefficient 73.3%[12] with D_c 1.448 Mg m^{-3}).[5]

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Footnotes

† Compound **2** was synthesized from 2-methoxyphenol **1** by oxidation with Fremy's salt [$(KSO_3)_2NO^\bullet$].[6] Yield 75%, mp 134 °C (decomp.). Satisfactory analytical data (^{1}H-, ^{13}C NMR, IR and MS) were obtained. Recrystallization of **2** from THF (0.1 g ml^{-1}) gave suitable single crystals.

‡ *Crystal data* for **2**: $C_7H_6O_3$, M = 138.12, orange–yellow crystal (0.12 × 0.25 × 0.25 mm), monoclinic, $P2_1/c$, a = 6.6497(7), b = 14.7216(7), c = 12.9417(12) Å, β = 90.81(1)°, Z = 8, D_c = 1.448 Mg m^{-3}, F(000) = 576, μ(Mo-Kα) = 1.1 cm^{-1}, 6555 reflections (θ < 27.5, ω/2θ scan, T = 150 K) were measured on an Enraf-Nonius CAD4T/rotating anode diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lp. The structure was solved by direct methods (SHELXS-86) and refined on F^2 by full-matrix least squares analysis (SHELXL-93) to R = 0.064, wR_2 = 0.137, S = 0.93; nonhydrogen atoms with anisotropic and hydrogen atoms with isotropic displacement parameters ($|\Delta\rho|$ < 0.29 e Å^{-3}). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, See Information for Authors, Issue No. 1.

§ 1 cal = 4.184 J and 1 D (Debye) = 3.33564 × 10^{-30} C m. MNDO[7] calculations; keywords PRECISE (geometry) followed by a Hessian calculation (keywords; FORCE and LARGE).[8]

¶ According to MNDO, **2** can be represented by a 'molecules-in-molecule' approach,[10] *viz.* **2** consists of the two coupled subunits acroleine {**3**; ΔH_f^0(**3**) −17.93 kcal mol^{-1},§ [O(n1)C(n1)C(n6)C(n5)]} and 3-methoxyacroleine {**4**; ΔH_f^0(**4**) −61.53 kcal mol^{-1},§ [O(n3)C(n4)C(n3)C(n2)O(n2)C(n7)]}. Bond lengths in Å and total atomic charges in q; **3**, O(n1)C(n1) 1.223, C(n1)C(n6) 1.488 and C(n5)C(n6) 1.342 and O(n1) −0.2926, C(n1) 0.2900, C(n5) 0.0070 and C(n6) −0.1824; **4**, O(n3)C(n4) 1.224, C(n3)C(n4) 1.480, C(n2)C(n3) 1.360, O(n2)C(n2) 1.350 and O(n2)C(n7) 1.404, and O(n3) −0.3051, C(n2) 0.1890, C(n3) −0.2954, C(n4) 0.3077, O(n2) −0.2873 and C(n7) 0.2083. Note that for **3** and **4** the numbering of **2** has been used (Fig. 1).

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