Pseudopolymorphic Crystals of Sodium Tetraphenyl-*p*-benzosemiquinone containing Two or Three Tetrahydropyran Solvent Molecules

Hans Bock,* Andreas John and Christian Näther

Chemistry Department, University of Frankfurt, Marie Curie Str. 11, D-60439 Frankfurt/Main, Germany

Single crystals of pseudopolymorphic modifications $[Ph_4C_6(O)_2^{\cdot-}Na^+(OC_5H_{10})_n]_\infty$ grow from tetrahydropyran solution (n = 2, orthorhombic, *Pcca*, Z = 4) or after equimolar addition of tetramethylethylendiamine (n = 3, monoclinic, $P2_1/c$, Z = 4) and provide information on subtle changes within the same structural motif in accord with the principle of dense lattice packing.

Conformational polymorphs of the same molecule,[1-3] together with quantum chemical calculations based on the X-ray structural data,[1] can shed light on intramolecular interactions which within the molecular degrees of freedom govern essential dynamic modes.[1] Pseudopolymorphic modifications of organic compounds,[2,3] *i.e.* those which differ in composition, are also of interest, especially if the difference is due to an 'innocent' solvent molecule, and if they provide clues concerning molecular self-organization.

Serendipitously, we have discovered that the contact ion pair[4,5] of tetraphenyl-*p*-benzosemiquinone radical anion with tetrahydropyran solvated Na^+ cation crystallizes differently from its tetrahydroyran solution after equimolar addition of tetramethylethylendiamine (TMEDA), although the latter is not incorporated into the crystal. Despite the either orthorhombic [Fig. 1(*a*)] or monoclinic [Fig. 1(*b*)] lattices, the dominant packing motif remains unchanged, in which the negatively charged oxygen centres of the semiquinone radical anions are connected by doubly tetrahydropyran–ether solvated Na^+ counterions and form infinite contact ion pair strings.

Based on the crystal data† of the pseudopolymorphic sodium tetraphenyl-*p*-benzosemiquinones with two or three tetrahydroyran (THP) solvent molecules (Fig. 1), their different lattice packing can be approximated as follows: Subtraction of the unit cell volumes† and division by Z = 4 yields (3831.4 − 3359.1)/4 = 118 pm^3 for the cavity filled by the third and non-bonded THP ether in the monoclinic lattice. For one THP molecule, literature increments[6] add up to its volume of 5(>CH_2) + 1(>O) = 5·16·76 + 8.63 = 92 pm^3. The quotient of these two values, V_{THP}/V_{Cavity} = 92/118 = 0.78, represents a cavity packing coefficient which, on comparison with usual values between 0.67 and 0.73,[6] indicates rather dense packing in the monoclinic pseudopolymorph with a clathrate-type inclusion of the additional third THP molecule. The packing coefficients, $c_K = \Sigma V_{molecules}/V_{unit\ cell}$, estimated from literature increments,[6] are 0.69 for the orthorhombic lattice with two THP ligands and 0.71 for the monoclinic lattice with three THP ethers, confirming its slightly higher density.† According to the principle of advantageous dense lattice packing[1-3] therefore, the monoclinic pseudopolymorphic modification should also contain the larger negative lattice (sublimation) energy.[1-3]

To rationalize the unexpected higher density of the monoclinic inclusion lattice, the ring centroid distances (in pm) are shown in Fig. 2.

The shortest of these nonbonded distances, between the centroid of tetrahydropyran selected in (1) and the centroids of the other rings, are 493 pm to benzoquinone radical anion with an interplanar angle of 75°, 526 pm to the Na^+ solvating ether ligands, 532 pm to the benzoquinone phenyl substituents and 614 pm between each other. Van der Waals interactions are treated in force field models often based on Lennard–Jones potentials, $E^{vdW} = cr^{-6} + dr^{-12}$, with the attractive dispersion dominating at longer distances.[7] For herringbone-type interactions, *e.g.* at statistically averaged distances of 505 pm and with interplanar angles 77°, lattice energy contributions of 5.4 kJ mol^{-1} result.[8] Therefore, and in close analogy with phenyl cluster nuclei often formed in proteins with phenyl-substituted amino acids such as phenylalanine,[8] it can be reasoned that the more dense monoclinic pseudopolymorphic lattice is favoured by the same principle.

For the influence of TMEDA, which despite its equimolar addition to the crystallization solution is not incorporated into the monoclinic lattice [Fig. 1(*b*)], quantum chemical calculations demonstrate that its complexing interaction[9] with Na^+[$\Delta\Delta H_f$(MNDO) = 391 kJ mol^{-1}] by far exceeds that of

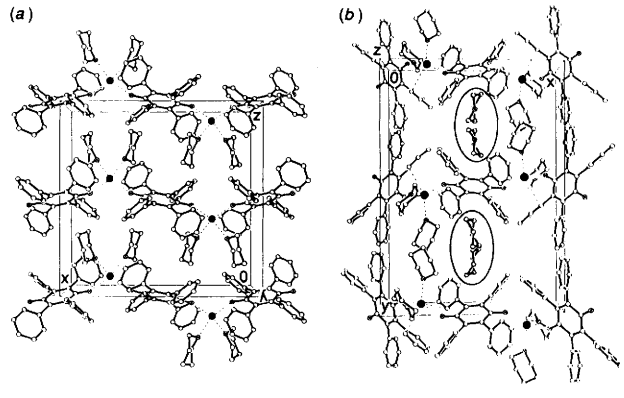

Fig. 1 Pseudopolymorphic modifications of tetraphenyl-*p*-benzosemiquinone sodium tetrahydropyran $[Ph_4C_6O_2^{\cdot-}Na^+(OC_5H_{10}O)_n]_\infty$. (*a*) Orthorhombic unit cell (*Pcca*, Z = 4) in y direction, exhibiting infinite chains of contact ion pairs between tetraphenyl-*p*-benzosemiquinone radical anions connected *via* twofold (n = 2) tetrahydropyran solvated Na^+ countercations. (*b*) Monoclinic unit cell ($P2_1/c$, Z = 4) in z direction, in which the contact ion pair strings are more strongly twisted (*e.g.* the interplanar angles between the quinone six-membered rings increase from 52 to 98°) and in which the enlarged crystal cavities are each filled with two additional (n = 3) tetrahydropyran molecules (encircled by shaded ellipsoids).

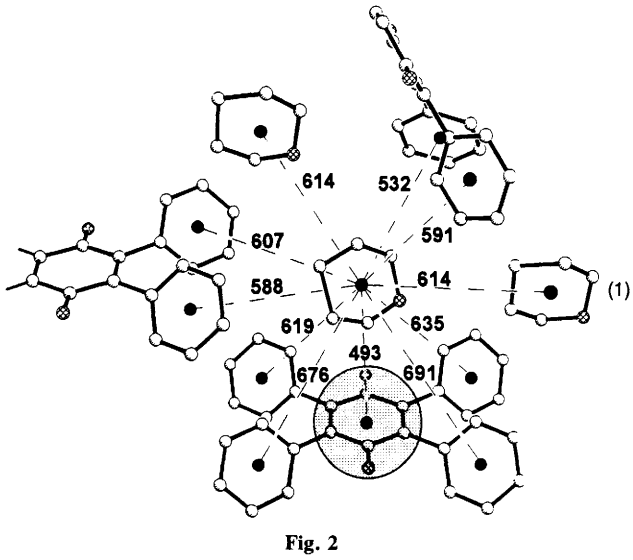

Fig. 2

ethers like the analogous dimethoxyethane [$\Delta\Delta H_f$(MNDO) = 296 kJ mol^{-1}], let alone tetrahydropyran with its large repulsion between the solvent molecules in octahedral Na^+ coordination.[10] Therefore, in tetrahydropyran solution the contact ion pair string between the tetraphenyl-*p*-benzosemiquinone radical anion and the counter cation [$Na^+(THP)_2$] is presumably preformed,[11] whereas the stronger Na^+ complexation by the added TMEDA ligand could allow a preferred formation of the more dense, strongly van der Waals interacting lattice.[12]

Received, 24th January 1994; Com. 4/00430B

Footnotes

† *Crystal data* for $C_{30}H_{20}NaO_2 \cdot 2C_5H_{10}O$: M = 607.71, orthorhombic, *Pcca*, a = 1761.6(1), b = 1102.4(1), c = 1729.7(1) pm, V = 3359.1 × 10^6 pm^3, T = 200 K, Z = 4, D_c = 1.202 g cm^{-3}, Mo-Kα radiation, λ = 71.073 pm, μ(Mo-Kα) = 0.09 mm^{-1}, 4442 measured reflections ($3 < 2\theta < 53°$), 3457 were independent and 2251 with $I > 2\sigma(I)$. Siemens AED 2 four-circle diffractometer, direct methods (SHELXTL PC). C, O, Na atoms anisotropically, H isotropically refined. 220 parameters, R = 0.0406, R_w = 0.0414, R_g = 0.0457, GOF = 1.9546, rest electron density = +0.24/−0.19 e Å^{-3}. Characteristic bond lengths (pm) and angles (°) for the contact ion pair [$Na^+TBQ^{\cdot-}(THP)_2$]: $Na^+\cdots O_{TBQ}$ 220, $Na^+\cdots O_{THP}$ 236, O_{TBQ}–Na–O_{TBQ} 110, O_{THP}–Na–O_{THP} 88, O_{TBQ}–Na–O_{THP} 155, O_{TBQ}–Na–O_{THP} 85.

Crystal data for $C_{30}H_{20}NaO_2 \cdot 3C_5H_{10}O$: M = 693.84, monoclinic, $P2_1/c$, a = 1595.2(1), b = 2236.5(3), c = 1085.6(1) pm, β = 98.41(1)°, V = 3831.4 × 10^6 pm^3, T = 150 K, Z = 4, D_c = 1.203 g cm^{-3}, Mo-Kα radiation, λ = 71.073 pm, μ(Mo-Kα) = 0.09 mm^{-1}, 7097 measured reflections ($3 < 2\theta < 50°$),. 6746 were independent and 5174 with $I > 2\sigma(I)$. Siemens AED 2 four-circle diffractometer, direct methods (SHELXTL PC). C, O, Na atoms anisotropically, H isotropically refined. 495 parameters, R = 0.0479, R_w = 0.0538, R_g = 0.0639, GOF = 2.9646, rest electron density = +0.46/−0.36 e Å^{-3} one THP molecule is disordered in one position and has been refined with a split model. Characteristic bond lengths (pm) and angles (°) for the contact ion pair [$Na^+TBQ^{\cdot-}(THP)_2$]: $Na^+\cdots O_{TBQ}$: 224, $Na^+\cdots O_{THP}$ 231, O_{TBQ}–Na–O_{TBQ} 156, O_{THP}–Na–O_{THP} 90, O_{TBQ}–Na–O_{THP} 97, O_{TBQ}–Na–O_{THP} 91, O_{TBQ}–Na–O_{THP} 93, O_{TBQ}–Na–O_{THP} 109.

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.

References

1 H. Bock, I. Göbel, C. Näther, Z. Havlas, A. Gavezzotti and G. Filippini, *Angew. Chem.*, 1993, **105**, 1823; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1755 and references cited therein.

2 J. Bernstein, *Conformational Polymorphism* in *Organic Solid State Chemistry*, ed. G. R. Desiraju, Elsevier, Amsterdam, 1987, pp. 474–518.

3 G. R. Desiraju, *Crystal Engineering* (*Mater. Sci. Monogr.*, 1989, 4), Elsevier, Amsterdam 1989, pp. 285–301, 42.

4 See, for example: H. Bock, *Jahrb. Akad. Dtsch. Naturf. Leopoldina*, LEOPOLDINA, 1993, **38**, 221; *J. Liq. Cryst. Mol. Cryst.*, 1994, in the press.

5 Review: H. Bock, K. Ruppert, C. Näther, Z. Havlas, H.-F. Herrmann, C. Arad, I. Göbel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel and B. Solouki, *Angew. Chem.*, 1992, **102**, 564; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 550.

6 See, for example: A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220, and references cited therein.

7 See, for example: G. Nemethy, M. S. Pottle and H. A. Sheraga, *J. Phys. Chem.*, 1983, **87**, 1883; Th. A. Halgren, *J. Am. Chem. Soc.*, 1992, **114**, 7827.

8 S. K. Burley and G. A. Petsko, *Science*, 1985, **229**, 23; *J. Am. Chem. Soc.*, 1986, **108**, 7995. See also C. A. Hunter, J. Singh and J. Thornton, *J. Mol. Biol.*, 1991, **218**, 837; C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525.

9 See, for example: E. Weiss, *Angew. Chem.*, 1993, **103**, 1565; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1501, and references cited therein.

10 H. Bock, C. Näther, Z. Havlas, A. John and C. Arad, *Angew. Chem.*, 1994, **106**, 931; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 875.

11 H. Bock, C. Näther, K. Ruppert and Z. Havlas, *J. Am. Chem. Soc.*, 1992, **114**, 6907.

12 See, for example: B. Collum, *Acc. Chem. Res.*, 1992, **25**, 448.