QUINONE OLIGOMERIZATION. AN X-RAY STUDY.

Jan-Eric Berg,[a] Holger Erdtman,[b] Hans-Erik Högberg,[b] Bengt Karlsson,[a] Anne-Marie Pilotti,[a]

Anne-Charlotte Söderholm[a]

[a]Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm,

S-104 05 Stockholm, Sweden

[b]Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Quinones of suitable structure undergo condensation reactions under the influence of strong acids with formation of complex dibenzofurans of the structural types 1-4.[1,2]
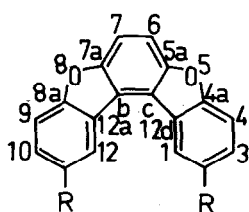
α-Naphthoquinone gives a cyclic tetramer in 90% yield.[1,3] 2,3-Dialkyl-p-benzoquinones give high yields (30-60%) of trimers and tetramers[4] and p-benzoquinone itself gives large amounts of black polymer together with a modest amount of the trimer 2b and minute amounts of other products including 3b[5] and 4a.
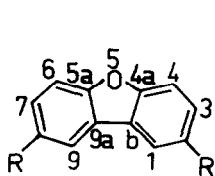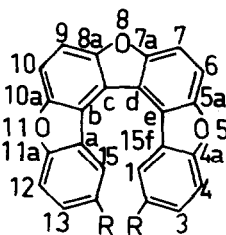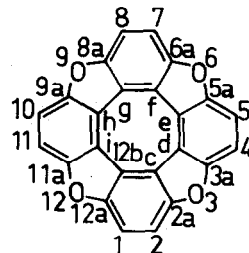

1a: R=H

1b: R=OH

1c: R=OCH₃

2a: R=H

2b: R=OH

2c: R=OCH₃

3a: R=H

3b: R=OH

4a

4b: Two H
instead
of one O

The NMR and mass spectra of the synthetic[6] compound 3a indicate that compounds of this type may be helical. When subjected to the Scholl reaction, compound 3a lost two hydrogen atoms and underwent cyclization to compound 4b.
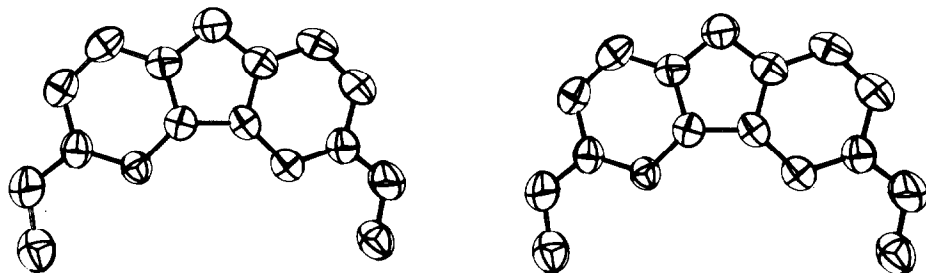
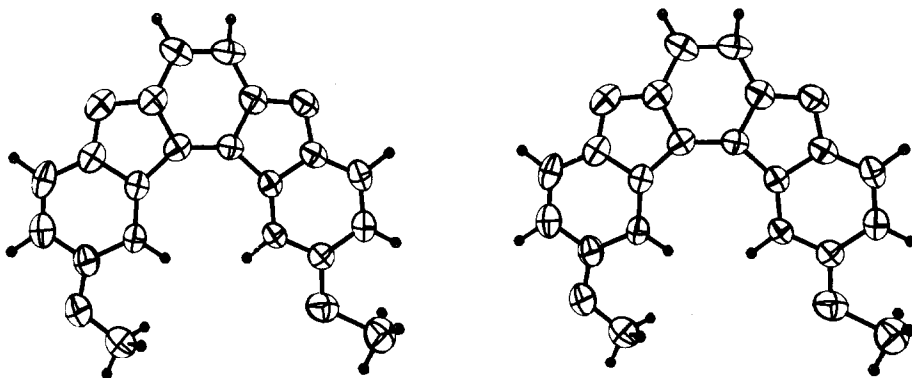Fig. 1. Stereoscopic view of the dimer 1c
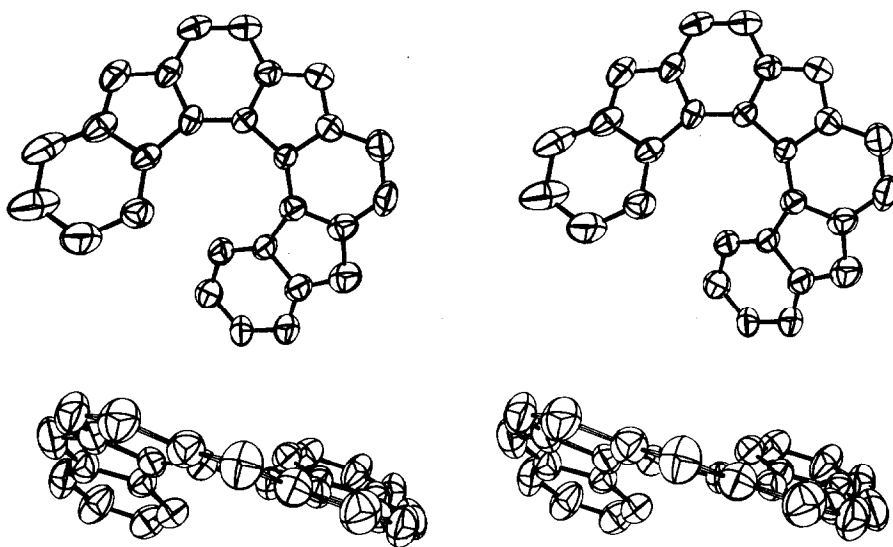

Fig. 2. Stereoscopic view of the trimer 2c

Fig. 3. Stereoscopic views of the open tetramer 3a from two directions

In order to check the possibility of a helical structure and to settle the question of whether or not compounds of type 4 are planar, crystallographic structures were determined for the compounds 1c, 2c, 3a and 4a.

The structures were solved by direct methods, using the programme MULTAN by Germain, Main and Woolfson.[7] Intensity data were measured on a computer-controlled Philips PW1100 diffractometer.

The dimer 1c crystallizes in the orthorhombic space group $P2_12_12_1$, with a = 21.230, b = 11.112, c = 4.805 Å, Z = 4. The molecule is planar to within $\pm$ 0.084 Å, i.e. significantly non-planar according to the positional standard deviations. Torsion angles calculated around the inner core of the molecule, i.e. the bonds C(1) – C(9b), C(9b) – C(9a) and C(9a) – C(9), are 176.8(0.6), 0.4(0.7), and –176.9(0.6)$^{\circ}$, respectively, showing that the molecule adopts a slight boat conformation. This is in accord with crystal structure studies of dibenzofuran.[8,9] The individual rings are not quite planar giving a dihedral angle of 4.0(2.0) between the benzene planes. A stereoscopic view of the molecule is shown in Fig. 1.

The trimer 2c crystallizes in the orthorhombic space group $P2_12_12_1$, a = 18.017, b = 15.031, c = 5.510 Å, Z = 4. The molecule is not quite planar; the interplanar angles vary from 0.8(0.4)$^{\circ}$ to 3.6(0.4)$^{\circ}$. The distortion from a planar configuration is probably partly a result of intra-molecular overcrowding between hydrogen atoms bonded to carbon atoms C(1) and C(12), see Fig. 2; these hydrogen atoms are bent away from each other so as to achieve a clearance of about 2.2 Å. This bending is distributed over the five fused rings in such a manner as to cause no severe buckling in any individual ring. The non-planarity of the trimer may be due in part to the fact that the dimer 1c is not planar. The methoxyl groups are oriented away from each other (Fig. 2) probably due to intramolecular interactions. The inner core aromatic bonds are lengthened relative to the parallel outer ones.

The open tetramer 3a crystallizes in the monoclinic space group $P2_1/c$ with a = 3.912, b = 20.406, c = 20.270 Å, β = 101.04°, Z = 4. The molecule has a helical structure (Fig. 3). The interplanar angle between the terminal rings is 37.3°. There is a pattern of shortened bond lengths along the periphery of the helix and lengthened bonds around the inner core of the molecule as has been shown in other helicenes.[10,11] Calculations of least-squares planes for each ring indicate that they deviate from planarity. The deviation is not as significant for the terminal rings as for the inner ones.

Without distortion from trigonal bonding the molecule would have an interacting carbon-carbon distance of about 1.4 Å. The short C...H intramolecular distances in the inner core of the molecule ($\simeq$ 2.5 Å) and the separation of 3.1 Å between the overcrowded carbon atoms C(1) and C(15) are achieved by adopting a helical configuration. The molecule is of point symmetry 2; the two-fold axis is not, however, a crystallographic two-fold axis.

The cyclic tetramer 4a (Crystal data: Space group $P2_1/c$, a = 3.745, b = 11.602, c = 16.597 Å, β = 93.87°, Z = 2, $i.e.$ only half a molecule in the asymmetric unit) has a planar configuration within experimental error (Fig. 4).
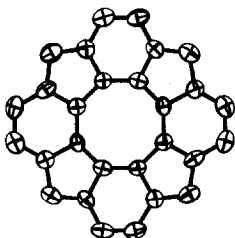

Fig. 4. Perspective view of the cyclic tetramer 4a.

REFERENCES

1. Erdtman, H., *Proc. Roy. Soc. (London)* A143 (1933) 228.

2. Erdtman, H.. and Högberg, H.-E., *Tetrahedron Lett.* 1970 3389.

3. Marschalk, C., *Bull. Soc. Chim.* (5)5 (1938) 304. Högberg, H.-E., *Acta Chem. Scand.* 26 (1972) 309.

4. Stjernström, N.E., *Arkiv Kemi* 21 (1963) 73. Högberg, H.-E., *Acta Chem. Scand.* 26 (1972) 2752.

5. Högberg, H.-E., unpublished.

6. Högberg, H.-E., *Acta Chem. Scand.* 27 (1973) 22.

7. G. Germain, P. Main and M.M. Woolfson, *Acta Cryst.* A27, 368 (1971).

8. O. Dideberg, L. Dupont and J.M. André, *Acta Cryst.* B28, 1002 (1972).

9. A. Banerjee, *Acta Cryst.* B29, 2070 (1973).

10. G.W. Frank, T. Hefelfinger and D.A. Lightner, *Acta Cryst.* B29, 223 (1973).

11. Th. E.M. van den Hark and J.H. Noordik, *Cryst. Struct. Comm.* 2, 643 (1973).