New type of quinone-quinone complexation in the reaction of 2,5-dichloro-1,4-benzoquinone with morpholine at high pressure

S. V. Chapyshev [a]* *and T. Ibata* [b]

[a] *Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588
[b] *Osaka University, Faculty of Science, Toyonaka, Osaka 560, Japan.*
Fax: (816) 853 7078

The complex of tetrakis(morpholino)-1,4-benzoquinone with 2,5-bis(morpholino)-1,4-benzoquinone of 2 : 1 stoichiometry was obtained in 9 % yield in the reaction of 2,5-dichloro-1,4-benzoquinone with morpholine at high pressure.

Key words: high pressure, aminoquinones, molecular complexes.

The main products of the reactions of 2,5-dichloro-1,4-benzoquinone (**1**) with amines under usual conditions are the corresponding 2,5-bis(amino)-3,6-dichloro-1,4-benzoquinones.[1] An increase in the reaction temperature favors nucleophilic substitution of chlorine atoms of **1** for amino groups and an increase in the yield of 2,5-bis(amino)-1,4-benzoquinones as minor products.[2] In this work, it is shown that the reaction of compound **1** with morpholine at high pressure results in the formation of trimolecular complex **6**, consisting of two molecules of tetrakis(morpholino)-1,4-benzoquinone (**2**) and one molecule of 2,5-bis(morpholino)-1,4-benzoquinone (**3**).

Results and Discussion

A new product, termolecular complex **6** (9 % yield, m.p. >350 °C), is formed as black microcrystals with typical metallic luster, along with known[2] bisaminoquinone **4** (46 % yield), in the reaction of quinone **1** with excess morpholine in THF at 50 °C and 600 MPa. The ^{1}H NMR and elemental analysis data testify[3] that complex **6** consists of two molecules of tetrakis(morpholino)-1,4-benzoquinone (**2**) and one molecule of 2,5-bis(morpholino)-1,4-benzoquinone (**3**), and this compound is not a simple mixture of aminoquinones **2** and **3**. Unlike free quinones **2** and **3** (Ref. 4), the UV spectrum of complex **6** exhibits only one intense band at 384 nm (ε 14800). It is of interest that no dissociation of complex **6** ($R_f = 0.47$) to the components (aminoquinones **2** ($R_f = 0.84$) and **3** ($R_f = 0.23$) is observed during its chromatographic separation on plates with silica gel (a 1 : 1 hexane—ethyl acetate mixture as eluent).

It can be assumed that the reaction of **1** with morpholine with morpholine at high pressure, like under normal conditions,[2] involves the formation of bisaminoquinones **3** and **4**. However, it is likely that at high pressure these quinones form trimolecular complex **5**, in which quinone **3** plays a role of a weak electron donor. The examples of such complexes are known,[5] and the capability of quinones of complex formation increases considerably as pressure increases.[6] The reaction of complex **5** with excess morpholine is likely the reason for the formation of complex **6**. The absence of free quinones **2** and **3** in the reaction products indicates that the amination of quinone **4** to derivative **2** occurs in the yield which should be expected in the case of preliminary complex formation of **3** with **4** followed by the amination of intermediate complex **5** to give derivative **6**. It is important that no complexation occurs when free quinones **2** and **3** are mixed in THF or MeCN or when these solutions are pressurized at 600 MPa. In addition, only quinones **3** and **4** in 9 and 50 % yields, respectively, are formed in the reaction of compound **1** with morpholine at somewhat lower pressure (400 MPa).

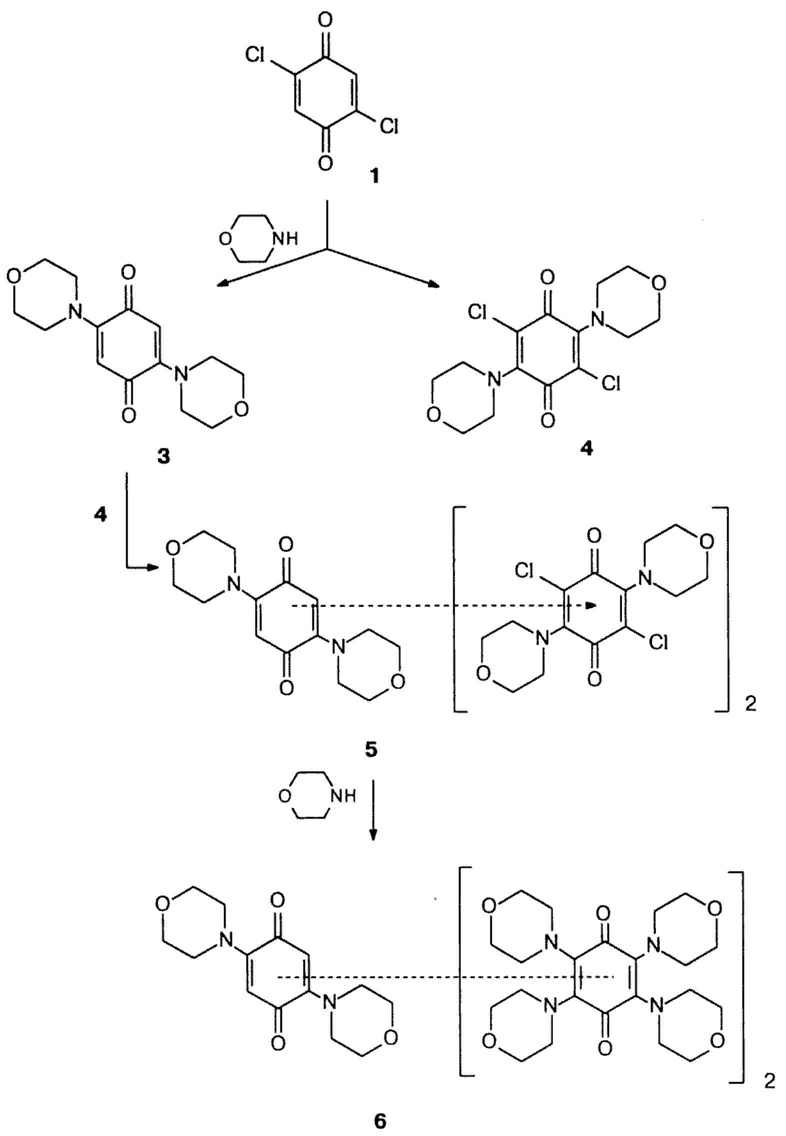
Taking into account a close structural analogy of complex **6** and the trimolecular complex of duroquinone with durene obtained recently,[7] it can be supposed that the crystalline structures of these complexes are similar. At the same time, product **6** obtained is a new type of the complexes in which both components are quinone molecules.

Experimental

NMR spectra were recorded on a JEOL EX-270 instrument (270 MHz for ^{1}H and 67.8 MHz for ^{13}C), using $SiMe_4$ as the internal standard. IR and UV spectra were recorded on Perkin-Elmer 983 and Hitachi U-3400 instruments. High-pressure reactions were carried out in a Teflon tube using a high-pressure Hikari Konatsu apparatus.[8]

Tetrakisaminoquinone (**6**) was prepared by the known procedure.[9]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 488—490, February, 1996.



Reaction of compound 1 with morpholine at high pressure. Morpholine (0.87 g, 10.0 mmol) was added to compound **1** (0.177 g, 1.0 mmol) in 5 mL of THF, the mixture obtained was pressurized for 48 h at 600 MPa and 50 °C, and then the solvent was distilled off at reduced pressure. A residue was chromatographed on a column filled with silica gel using a hexane—ethyl acetate (1 : 1) system as the eluent. Compound **4** (53 mg, 46 % yield) was obtained, $R_f = 0.71$, m.p. 202—204 °C (see Ref. 2); 21 mg (9 %) **6**, $R_f = 0.47$, m.p. >350 °C. UV-Vis (CH_2Cl_2), λ_{max}/nm (ε): 384 (14800). IR (KBr), ν_{max}/cm^{-1}: 2956, 2917, 2849, 1627, 1562, 1550, 1449, 1408, 1370, 1315, 1297, 1266, 1238, 1201, 1147, 1114, 1093, 1066, 1024, 1003, 986, 937, 881, 851, 753. ^{1}H NMR ($CDCl_3$), δ: 5.53 (s, 2 H, H(3) and H(6)); 3.78 (m, 8 H, OCH_2); 3.75 (m, 32 H, OCH_2); 3.54 (m, 8 H, NCH_2); 3.29 (m, 32 H, NCH_2). ^{13}C NMR ($CDCl_3$), δ: 183.1 (C′(1)); 182.7 (C(1)); 152.3 (C(2)); 139.1 (C′(2)); 107.0 (C(3)); 67.4 (OCH_2′); 66.4 (OCH_2); 51.0 (NCH_2′); 49.0 (NCH_2). Found (%): C, 59.50; H, 7.24; N, 11.71. $C_{58}H_{82}N_{10}O_{16}$. Calculated (%): C, 59.27; H, 7.03; N, 11.92.

References

1. A. Kotyrev, *Tetrahedron*, 1991, **47**, 8043.
2. R. A. Henry and W. M. Dean, *J. Am. Chem. Soc.*, 1952, **74**, 278.
3. R. Foster and M. I. Foreman, *The Chemistry of the Quinonoid Compounds*, Ed. S. Patai, Wiley, London, 1974, Pt. 1, 257.
4. K. Wallenfels and W. Draber, *Tetrahedron*, 1964, **20**, 1889.
5. R. L. Hansen, *J. Org. Chem.*, 1968, **33**, 3968.
6. A. H. Ewald, *Trans. Faraday Soc.*, 1968, **64**, 733.
7. H. Koshima, Y. Chisaka, Yang Wang, Xin Kan Yao, Honggen Wang, Ruji Wang, A. Maeda, and T. Matsuura, *Tetrahedron*, 1994, **50**, 13617.
8. K. Matsumoto, A. Sera, and T. Uchida, *Synthesis*, 1985, 1.
9. K. Wallenfels and W. Draber, *Justus Liebigs Ann. Chem.*, 1963, **667**, 55.

Received July 13, 1995