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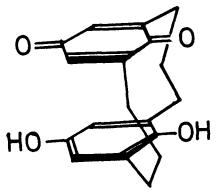
CHARGE TRANSFER INTERACTION IN [3.3]METACYCLOPHANE QUINHYDRONE[1)]

Teruo SHINMYOZU, Takahiko INAZU, and Tamotsu YOSHINO
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812

syn-[3.3]Metacyclophane quinhydrone 1 was synthesized by oxidation of bisphenol 6 with thallium trifluoroacetate,[2)] followed by catalytic hydrogenation. The quinhydrone 1 showed a characteristic broad CT absorption in the region of 350-600 nm with a maximum at 446 nm (ε2510) in dioxane.

In the study on [3.3]cyclophanequinones,[3)] we observed that the meta- and meta-paracyclophane systems adopted less suitable conformations to the CT interaction than that of the paracyclophane system. However, the CT bands of the former were submerged in the intensive π-π^* band of the benzoquinone chromophore itself. So we intended to synthesize [3.3]cyclophane quinhydrones in order to obtain more detailed information regarding the CT interaction in [3.3]meta- and [3.3]metaparacyclophane systems. Now we wish to report the synthesis and CT interaction in [3.3]metacyclophane quinhydrone 1. In paracyclophane quinhydrones, H.A.Staab et al. have synthesized various quinhydrones and investigated the orientation and distance dependence of CT interactions.[4)] S.Misumi et al. have synthesized triple- and quadruple-layered paracyclophane quinhydrones.[5)]



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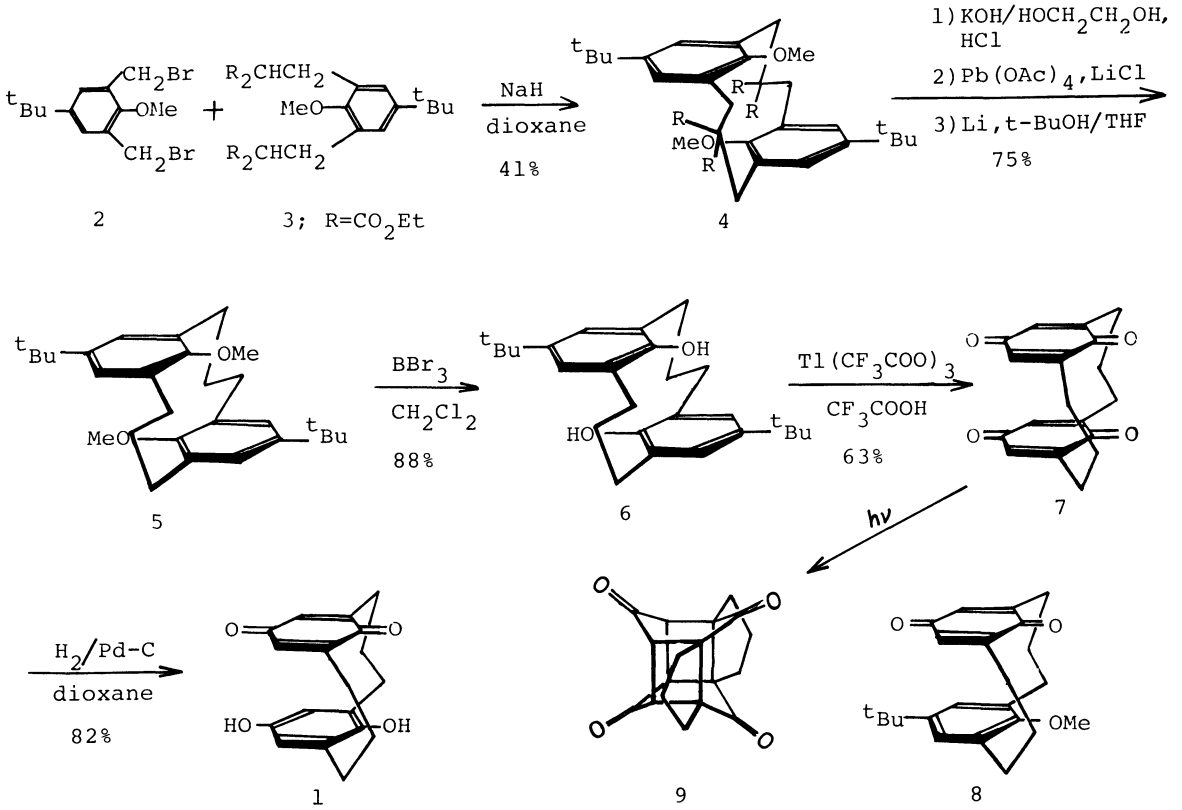
2,6-Bis(bromomethyl)-4-t-butylanisole 2[6)] and tetraester 3 were coupled in the presence of NaH in refluxing dioxane to give cyclic tetraester 4 in 41% yield. The compound 4:[7)] colorless needles from CCl_4, mp 264.5-265°. Pmr($CDCl_3$): 1.28(s,18H,t-Bu), 1.38(t, J=8Hz,12H,$-CH_2\underline{CH_3}$), 3.16(s,6H,$-OCH_3$), 3.28(ABq,J=16Hz,8H,$ArC\underline{H_2}-$), 4.37(q, J=8Hz,$-\underline{CH_2}CH_3$), 6.95(s,4H,ArH). The cyclic tetraester 4 is considered to be fixed to an anti conformation by the following reasons: (1) the methoxy methyl protons exhibited higher field shifts by 0.63 ppm, whereas both the aromatic protons and the t-butyl protons did not show such high field shifts compared with those of the tetraester 3; (2) no conformational change was observed even after refluxing the decalin solution of 4 for 11h. Therefore the product is exclusively the anti conformer. The ester 4 was decarboxylated by the usual methods[8)] to give 5 in 75% yield. The compound 5: colorless crystals from EtOH, mp 209-211°. Pmr($CDCl_3$): 1.32(s,18H,t-Bu), 1.8-2.9(m,12H, $-CH_2CH_2CH_2-$), 3.11(s,6H,$-OCH_3$), 6.96(s,4H,ArH). The bisether 5 was demethylated by BBr_3 in CH_2Cl_2 at room temp to give bisphenol 6 in 88% yield. The compound 6: colorless crystals from CH_2Cl_2, mp 187-190°. Pmr($CDCl_3$): 1.33(s,18H,t-Bu), 1.9-2.9(m,12H, $-CH_2CH_2CH_2-$), 7.07(s,4H,ArH). The pmr spectrum showed that the bisphenol 6 still adopted the anti conformation; no conformational change was observed in the decarboxylation and in the demethylation. The bisphenol 6 was treated with thallium trifluoroacetate in trifluoroacetic acid at room temp for 13h to give bisquinone 7 in 63% yield. The compound 7: orange needles from CH_2Cl_2, dec$>$ 230°. Found: C, 72.76;

H, 5.38%; mol wt (MS,M^+) 296. Calcd for $C_{18}H_{16}O_4$: C, 72.96, H, 5.44%; mol wt 296. Pmr: 1.8-3.4(m,12H,$-CH_2CH_2CH_2-$), 6.70(s,4H,olefinic H) in CF_3COOH; 1.5-3.2(m,12H,$-CH_2-CH_2CH_2-$), 6.38(s,4H,olefinic H) in $CDCl_3$; $\nu_{c=o}$ 1650 cm^{-1}(KBr). The olefinic protons of 7 appeared as a singlet at 6.38 ppm in $CDCl_3$ and showed no temperature dependence up to +180° in DMSO-d_6. Whereas the absorption due to trimethylene bridges appearing as complex multiplets between 2.3-4.0 ppm at room temp became two multiplets centered on ca 2.0 (4H,$-CH_2\underline{CH_2}CH_2-$) and 2.5 ppm (8H,$-\underline{CH_2}CH_2\underline{CH_2}-$) above +130° in DMSO-$d_6$. This phenomenon as well as the fact that 7 is converted into the photoisomer 9 by [2+2] cycloaddition suggests that the syn and anti conformers are at equilibrium and the syn conformer is converted into the photoisomer 9. But the unambiguous information on the conformation was not obtained, for the low temperature pmr spectrum of 7 could not be measured because of its limited solubility in solvents.

The bisquinone 7 was sensitive to light and slowly converted into the colorless photoisomer 9 by scattering light. The more smooth conversion was attained by irradiating the $CHCl_3$ solution with a high pressure mercury lamp. The compound 9: colorless fine needles from dioxane, dec > 280°. Pmr(CF_3COOH): 1.6-2.6(m,12H,$-CH_2CH_2CH_2-$), 3.68 (s,4H,>CH-); $\nu_{c=o}$ 1690 cm^{-1} (KBr).

In the synthesis of 7, a small amount of 8 was obtained as a by-product. The formation of 8 was probably due to incomplete demethylation and following oxidation.

The compound 8: yellow needles from CH_2Cl_2, mp 127.5-129°. Pmr($CDCl_3$): 1.16(s,9H, t-Bu), 1.5-3.3(m,12H,$-CH_2CH_2CH_2-$), 3.57(s,3H,$-OCH_3$), 5.89(s,2H,olefinic H), 6.84(s,2H,



Scheme 1

ArH); $\nu_{c=o}$ 1650 cm^{-1} (KBr). The olefinic proton showed similar chemical shift as that of [3.3]metacyclophanequinone which adopted the syn conformation,[3] and both of the olefinic protons and the aromatic protons showed no temperature dependence to +180° in DMSO-d_6. Consequently, 8 is considered to adopt the syn conformation.[9]

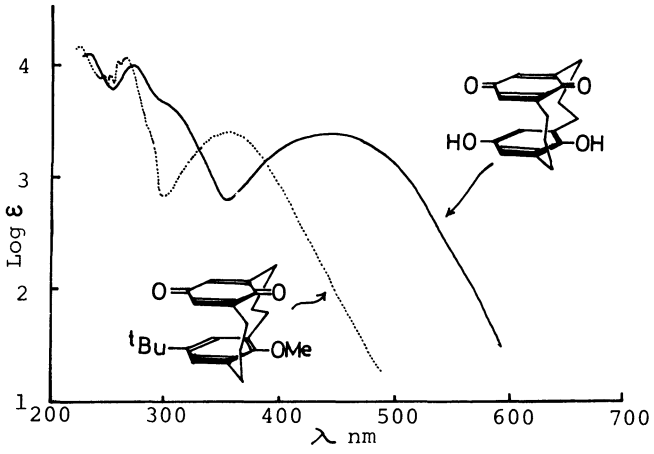


Fig. 1. Electronic spectra of 1 and 8 in dioxane

The bisquinone 7 was catalytically hydrogenated over 5% Pd-C in dioxane at room temp to give the desired quinhydrone 1 in 82% yield. The compound 1: glittering black crystals from THF-benzene, dec > 230°. Found: C, 72.34; H, 6.06%; mol wt (MS,M^+) 298. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08%; mol wt 298. Pmr(DMSO-d_6): 1.3-3.2(m,12H,-$CH_2CH_2CH_2$-), 5.93(s,2H, olefinic H), 6.10(s,2H,ArH), 7.5-7.8(m,-OH); $\nu_{c=o}$ 1630; ν_{OH} 3450, 3230 cm^{-1} (KBr).

The higher field shift of the olefinic protons of 1 than that of 2,6-dimethyl-p-benzoquinone (6.62 ppm in DMSO-d_6) suggests that 1 adopts the syn conformation. In fact, both of the olefinic protons and the aromatic protons of 1 have similar chemical shifts as those of pseudogeminal [3.3]paracyclophane quinhydrone.[10] The two singlets of the olefinic protons and the aromatic protons of 1 remained unchanged up to +100° in DMSO-d_6. Moreover bishydroquinone, which was prepared by catalytic hydrogenation of the bisquinone 7, was exclusively the syn conformer. Therefore, 1 is considered to be fixed to the syn conformation up to +100°. In [3.3]metacyclophane, the syn conformation was found to be more stable than the anti one.[11] The fixation to the syn conformation in 1 was ascribed to additional stabilization of the syn conformer by CT interaction as found in [3.3]metacyclophanequinone.[3]

The electronic spectra of 1 and 8 are shown in Fig. 1. The quinhydrone 1 shows a characteristic broad CT band at 446 nm (ε2510) in dioxane. The absorption curve of 1 resembles that of pseudogeminal [3.3]paracyclophane quinhydrone rather than that of pseudoortho [3.3]paracyclophane quinhydrone.[10] This suggests that 1 takes the similar orientation of a donor and an acceptor as that of pseudogeminal [3.3]paracyclophane quinhydrone. As expected, the CT interaction in 1 is significantly stronger than that in [3.3]metacyclophanequinone. The position and extinction of the CT band of 1 suggest that its CT interaction is considerably strong but is weaker than in pseudogeminal [3.3]paracyclophane quinhydrone. This is attributed to the fact that the former has a superposed conformation but is slightly deviated from the parallel stacking of a donor and an acceptor moieties, whereas the latter has a well superposed conformation and the parallel stacking of a donor and an acceptor moieties. The CT band of the quinone 8 appears at 353 nm (ε2430) in dioxane and shows a marked hypsochromic shift as compared with that of 1. This is attributed to the weaker π-basicity of 2,6-dimethyl-4-t-butylanisole than that of 2,6-dimethyhydroquinone, and the steric hindrance of t-butyl group: the TCNE complex of the former shows the CT band at 460 nm, whereas that of dimethyl ether of the latter appears at 589 nm in CH_2Cl_2.

Synthetic studies of [3.3]metaparacyclophane quinhydrones are now in progress.

References and notes

1) We are especially grateful to Professor H.A.Staab for sending us a copy of his paper prior to publication. From his private communication, he reported the synthesis and CT interaction of the title compound at "Gorden Research Conference, Electron Donor-Acceptor Interaction", the Brewster Academy, Wolfeboro, New Hampshire, USA, August, 1978, and submitted for publication to both Tetrahedron Lett. and Chem.Ber.. But we wish to report the synthesis of the title compound, for the approach was different from his and involved the novel method for preparing the bisquinone 7 from the bisphenol 6.

2) A.McKillop, B.P.Swann, and E.C.Taylor, Tetrahedron, 26, 4031 (1970).

3) T.Shinmyozu, T.Inazu, and T.Yoshino, Chem.Lett., 1977, 1347; 1978, 1319.

4) W.Rebafka and H.A.Staab, Angew.Chem., 85, 831 (1973), 86, 234 (1974); Angew.Chem. Int.Ed.Engl., 12, 776 (1973); 13, 203 (1974). H.A.Staab and W.Rebafka, Chem.Ber., 110, 3333 (1977). H.A.Staab and C.P.Herz, Angew.Chem., 89, 406 (1977); Angew.Chem. Int.Ed.Engl., 16, 392 (1977). Idem, Angew.Chem., 89, 839 (1977); Angew.Chem.Int.Ed. Engl., 16, 799 (1977). R.Reimann and H.A.Staab, Angew.Chem., 90, 385 (1978); Angew. Chem.Int.Ed.Engl., 17, 374 (1978). H.A.Staab and V.Schwendermann, Angew.Chem., 90, 805 (1978); Angew,Chem.Int.Ed.Engl., 17, 756 (1978). H.A.Staab and U.Zapf, Angew. Chem., 90, 807 (1978); Angew.Chem.Int.Ed.Engl., 17, 757 (1978). H.A.Staab, U.Zapf, and A.Gurke, Angew.Chem., 89, 841 (1977); Angew.Chem.Int.Ed.Engl., 16, 801 (1977).

5) H.Machida, H.Tatemitsu, Y.Sakata, and S.Misumi., Tetrahedron Lett., 1978, 915.

6) This compound was readily prepared by the bromomethylation of t-butylanisole.

7) Satisfactory elemental analyses and mass spectral data were obtained for 4, 5, 8, and 9.

8) T.Shinmyozu, T.Inazu, and T.Yoshino., Chem.Lett., 1976, 1405; 1977, 1347.

9) A referee pointed out that the pmr data alone were insufficient to establish the conformation of 8 and the possibility of the anti conformation should be considered because of the steric hindrance of t-butyl group.

10) H.A.Staab and C.P.Herz, Angew.Chem., 89, 839 (1977); Angew.Chem.Int.Ed.Engl., 16, 799 (1977).

11) T.Shinmyozu, T.Inazu, and T.Yoshono, unpublished results.

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