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A CONFORMATIONAL STUDY OF THREE ISOMERIC [3.3]CYCLOPHANEQUINONES*

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Three isomeric [3.3]cyclophanequinones 2-4 were synthesized. The conformations of these compounds were discussed on the basis of the NMR spectra. The electronic spectra suggested that the paracyclophane system adopted the most suitable conformation for charge transfer interaction.

In the previous paper[1] we reported the synthesis of [3.3]paracyclophane-5,8-quinone (1) which showed a characteristic broad CT band at 406 nm in acetonitrile. We were interested in studying on the influence of the relative orientation of a benzene and a benzoquinone moiety on CT interaction in the [3.3]cyclophanequinone[2] system.

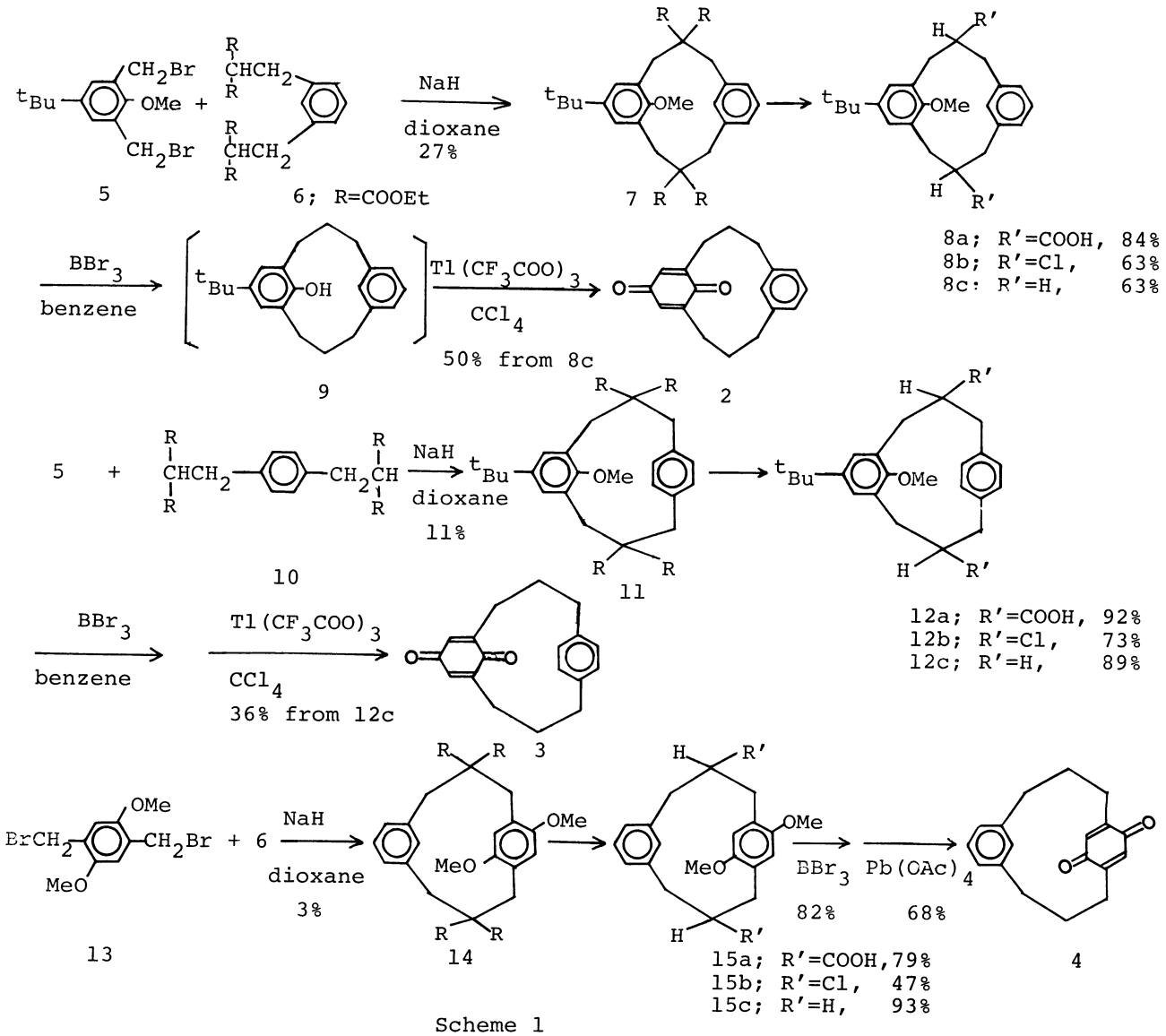
Recently S. Misumi et al. reported the interesting phenomenon that the meta-cyclophane system exhibits the most intensive CT band in [2.2]tropyliocyclophanes.[3] Now we wish to report the syntheses of three isomeric [3.3]cyclophanequinones: [3.3]metacyclophane-6,9-quinone (2), [3.3]metaparacyclophane-6,9-quinone (3), and [3.3]metaparacyclophane-14,17-quinone (4).

2,6-Bis(bromomethyl)-4-t-butylanisole (5), which was readily prepared by the bromomethylation of 4-t-butylanisole, and tetraester 6 were coupled in the presence of NaH in refluxing dioxane to give cyclic tetraester 7 in 27% yield. The ester 7 was considered to adopt an anti conformation[4] because both the inner aromatic proton and the methoxy protons exhibited higher field shifts by 0.77 and 0.17 ppm compared with those of 2,6-dimethyl-4-t-butylanisole, respectively. The ester 7 was hydrolyzed into diacid 8a under alkaline conditions in 84% yield. The acid 8a was treated with lead tetraacetate and LiCl in pyridine-HMPA at 90° for 1h to give dichloride 8b in 63% yield. The dichloride 8b was reduced with lithium and t-butanol in refluxing THF to give 6-t-butyl-9-methoxy[3.3]metacyclophane (8c) in 63% yield. 8c: colorless needles from ethanol, mp 134.5-135.5°. The inner aromatic proton of 8c occurring at 7.23 ppm shifted markedly to lower field by 1.1 ppm as compared with that of 7. Furthermore, the chemical shift of the inner aromatic proton showed no temperature dependence between -90°(CD_2Cl_2) and +150°(DMSO-d_6). These results indicated that 8c was fixed to a syn conformation. The metacyclophane 8c was demethylated by BBr_3 in refluxing benzene and resulting t-butylphenol derivative 9 was treated with anhydrous thallium trifluoroacetate in refluxing CCl_4 for 10h to give desired quinone 2 in 50% yield from 8c according to the method developed by McKillop et al.[5] 2: yellow needles by sublimation, mp 147.5-148.5°.

By the coupling reaction of dibromide 5 and ester 10, cyclic tetraester 11 was

obtained in 11% yield. The aromatic protons of para-bridged ring of 11 exhibited a pair of multiplets at 6.40 and 6.91 ppm with equal intensity. Therefore both rotation of the para-bridged ring and inversion of the meta-bridged ring were assumed to be restricted. The ester 11 was decarboxylated by the usual methods described above to give 12c in 60% yield from 11. 12c: colorless needles from ethanol, mp 115-116°. Similarly, the aromatic protons of para-bridged ring of 12c appeared unequivalently at 6.06 and 6.94 ppm with equal intensity. This unequivalence was attributed to the fixed conformation. [3.3]Metaparacyclophane-6,9-quinone (3) was obtained in 36% yield from 12c. 3: yellow needles by sublimation, mp 121.5-122.5°. [3.3]Metaparacyclophane-14,17-quinone (4) was synthesized by a similar procedure as described in Scheme 1. The aromatic and the methoxy methyl protons of 14 appeared as singlet, respectively. Therefore the meta-bridged ring was considered to be inverted rapidly at room temperature. 4: yellow crystals by sublimation, mp 115-118°.[6)]

The NMR spectral data are shown in Fig. 1. The olefinic protons of the metacyclophanequinone 2 showed a higher field shift compared with those of the other quinones and the spectrum was temparature independent between -70 (CD_2Cl_2) and +200°



Scheme 1

(Hexachlorobutadiene). These data suggested that 2 was fixed to the syn conformation as depicted in Fig. 2. In [3.3]metacyclophane, the syn conformation was found to be more stable than the anti one and the energy barrier for the ring inversion was estimated to be ca. 11 kcal/mol.[7] The fixation to the syn conformation in 2 was ascribed to additional stabilization of the syn conformer by CT interaction.

The aromatic protons of 3 appeared as a pair of multiplets at 6.90 and 7.00 ppm at room temperature. The unequivalence of the protons suggested that both benzene ring rotation and benzoquinone ring inversion were restricted. On the other hand, the olefinic protons of 4 appeared as singlet at 6.20 ppm. Therefore, the benzene ring was assumed to be inverted rapidly at room temperature in 4. The energy barrier for the benzene ring inversion in parent [3.3]metaparacyclophane was estimated below 8 kcal/mol by low temperature NMR spectrum.[8]

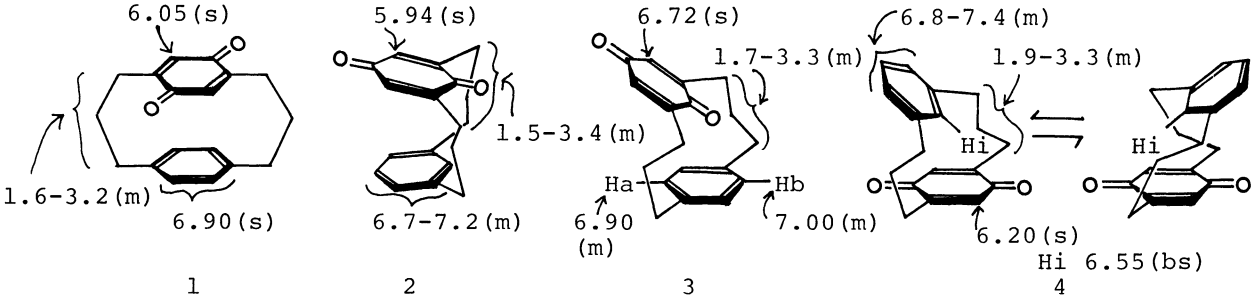


Fig. 1. NMR spectra in $CDCl_3$.

The inner aromatic proton(Hi) of 4 occurring at 6.55 ppm, which was located over the center of the benzoquinone ring, shifted only slightly to higher field. Moreover, the difference of the chemical shifts of two kinds of aromatic protons of 3 was only 0.1 ppm, whereas that of the compound 12c was 0.88 ppm.

The electronic spectra of the compounds 1-4 are shown in Fig. 2. The compounds 2-4 did not show any maxima of the CT bands, though 1 showed a characteristic broad CT band at 406 nm. The bands of 2-4 were considered to be submerged with the intensive π-π^* band, because these bands became less intensive and shifted to shorter wave length region than that of 1. These observations suggested that the CT interaction in the metacyclophane 2, structure of which has a superposed conformation but was deviated from the parallel stacking of a donor and an acceptor moieties, was weaker than that in the paracyclophane 1. In the case of the metaparacyclophanequinone, which has a partially superposed conformation and was deviated from the parallel stacking, the CT interaction was also weaker than that of 1. Therefore, we conclude that the paracyclophane system, which has a parallel and near center-on-center stacking of a donor and an acceptor moieties, adopted the most suitable conformation to the CT interaction in [3.3]cyclophanequinones. This result was in fair agreement with those of the theoretical calculations by C. K. Prout et al.[9]

References and notes

NMR($CDCl_3$,δ) data.
7:1.21(9H,s,t-Bu), 1.38(12H,dt,$-CH_2\underline{CH_3}$), 3.22(4H,s,benzylic H), 3.42(4H,ABq, J=15Hz, benzylic H), 3.50(3H,s,-OMe), 4.36(8H,dq, $-\underline{CH_2}CH_3$), 6.90(3H,bs,outer arom H), 6.13 (1H,bs,inner arom H), 7.03(2H,s,arom H).
8c: 1.10(9H,s,t-Bu), 3.68(3H,s,-OMe), 6.57(2H,s,arom H), 6.4-6.8(3H,m,outer arom H), 7.23(1H,m,inner arom H), 1.5-3.4 (12H,m,$-CH_2CH_2CH_2-$).
11: 1.19(9H,s,t-Bu), 1.34(12H,dt,$-CH_2\underline{CH_3}$), 3.27(3H,s,-OMe), 4.26(8H,dq,$-CH_2-$), 6.40 and 6.91(4H,m,arom H), 6.63(2H,s,arom H), ca. 3.25(4H,m,benzylic H), 3.27(4H,ABq, J= 15Hz,benzylic H). 12c: 1.30(9H,s,t-Bu), 2.0-3.0(12H,m,$-CH_2CH_2CH_2-$), 3.28(3H,s,-OMe), 6.06 and 6.94(4H,m,arom H), 6.80(2H,s,arom H). 14: 1.33(12H,t,$-CH_2\underline{CH_3}$), 3.50(6H,s, -OMe), 2.8-3.9(8H,m,benzylic H), 4.32(8H,dq,$-\underline{CH_2}CH_3$), 5.65(1H,m,inner arom H), 6.43 (2H,m,arom H), 6.6-7.1(3H,m,outer arom H).

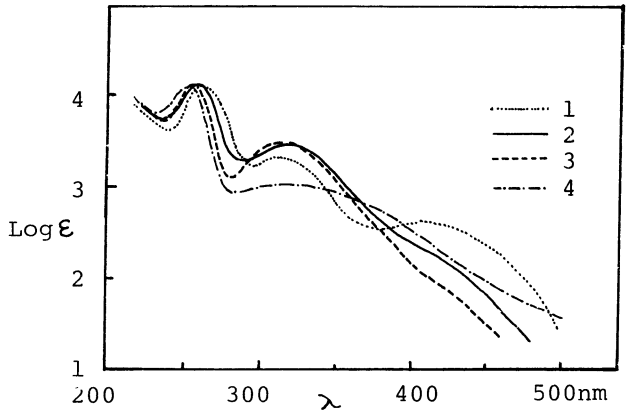


Fig. 2.
Electronic spectra of 1-4 in acetonitrile.

1) T. Shinmyozu, T. Inazu, and T. Yoshino, Chem. Lett., 1977, 1347.
2) A number of cyclophanequinones and cyclophanequinhydrones have been synthesized.
a) D. J. Cram and A. C. Day, J. Org. Chem., 31, 1227 (1966). b) D. J. Cram and R. A. Reeves, J. Am. Chem. Soc., 80, 3094 (1958). c) H. Tatemitsu, T. Otsubo, Y. Sakata, and S. Misumi, Tetrahedron Lett., 1975, 3059. d) Reference 1. e) W. Rebafka and H. A. Staab, Chem. Ber., 110, 3333 (1977). f) H. Vogler, G. Ege, and H. A. Staab, Tetrahedron, 31, 2441 (1975). g) H. A. Staab and C. P. Herz, Angew. Chem., 89, 839 (1977). h) H. A. Staab, C. P. Herz, and H. -E. Henke, Chem. Ber., 110, 3351 (1977). i) H. A. Staab, U. Zopf, and A. Gurke, Angew. Chem., 89, 841 (1977). j) H. A. Staab and C. P. Herz, Angew. Chem., 89, 841 (1977). k) H. Machida, H. Tatemitsu, Y. Sakata, and S. Misumi, Tetrahedron Lett., 1978, 915. l) A. R. Forrester and R. Ramasseul, J. Chem. Soc.(B), 1971, 1638. m) H. A. Staab and C. P. Herz, Angew. Chem., 89, 406 (1977). Angew. Chem., Int.Ed. 16, 392 (1977).
3) H. Horita, T. Otsubo, and S. Misumi, Chem. Lett., 1977, 1309.
4) In [3.3]metacyclophane system, the product obtained in the coupling reaction had exclusively the anti conformer.
5) A. McKillop, B. P. Swann, and E. C. Taylor, Tetrahedron, 26, 4031 (1970).
6) All new compounds gave satisfactory elemental analyses and mass spectral data.
7) T. Shinmyozu, T. Inazu, and T. Yoshino, unpublished results.
8) K. Tomiyoshi, T. Shinmyozu, T. Inazu, and T. Yoshino, unpublished results.
9) B. Mayoh and C. K. Prout, J. Chem. Soc., Faraday trans 2, 68, 1072 (1972).
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