

>308°C, MS(m/e): 104 (100%), 238 (17%) and 476 (0.6%, M⁺), IR (KBr) $\nu_{C=O}$ 1702 (m), 1662 (s) and $\nu_{C=C}$ 1616 (m) cm⁻¹] at room temperature in the dark; heating accelerated the conversion. The dimer was probably formed by the Diels-Alder reaction. Further elucidation of its structure was not possible because it was practically insoluble in all the solvents tested.

The color of the solution of **2** was markedly solvent dependent (brown and violet in nonpolar and polar solvents, respectively).

As shown in Figure, the shoulders at the longest wavelength region are subject to hypsochromic shifts in polar solvents (n- τ^*). The absorption maxima of **1** and **2** around 500 nm are assigned as the intramolecular CT bands due to the transannular interaction between the o-benzoquinone and benzene rings on the basis of the solvent effect [λ_{max} , nm (ϵ ,

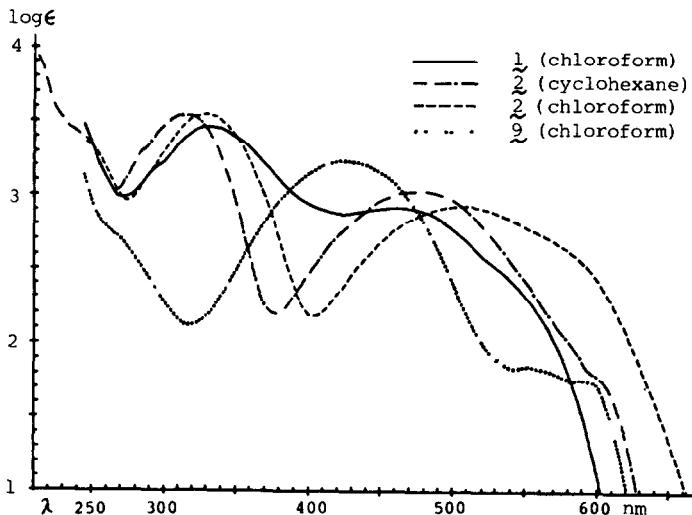


Figure The electronic spectra of **1**, **2** and **3**

solvent), **1** 439 (996, cyclohexane),

459 (833, CH₃CN) and 461 (843, CHCl₃), **2**: 476 (1070, cyclohexane), 503 (865, CH₃CN) and 507

(858, CHCl₃) and the considerable shift to the longer wavelength in going from the [2.2]- to the more favorable [3.3]phane system. The behavior of these bands is similar to that of the CT bands of the corresponding cyclophane-p-quinones^{3,7}. The assignment is also supported by the marked red shift of the band upon introduction of an electron-rich t-butylamino group into the benzene ring of **1** (λ_{max} 605 nm)².

REFERENCES AND NOTES

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- 5) Because of instability **2** could not be obtained pure by oxidation of 2,5-dimethylphenol with **4**. The oxidation of 3,6-dimethylcatechol with AgCO₃/Celite gave analytically pure **2** in 96% yield, red prisms, mp 81.5-83°C, decomposed on standing at room temperature.
- 6) Satisfactory elemental analyses were obtained for all the new compounds. Spectral data are as follows [IR (CH₂Cl₂, $\nu_{C=O}$, cm⁻¹), ¹H-NMR (CDCl₃, 60 MHz, δ , ppm)]
 - 1**: IR, 1667; ¹H-NMR, 6.92, 6.50 (m, ArH), 5.90 (s, quinone), and 2.0-3.3 (m)
 - 2**: IR, 1676 (w), 1659 (s), ¹H-NMR, 7.12, 6.93 (m, ArH), 6.10 (s, quinone), and 1.6-3.2 (m)
 - 3**: IR, 1655 (s), 1650 (s), ¹H-NMR, 7.1-7.6 (m, PhSe), 6.88 (AA'BB'm, ArH), 6.00 (s, quinone) and 1.7-3.1 (m), MS, M⁺ 422.
 - 9**: IR, 1681 (w), 1659 (s), ¹H-NMR, 6.70 (s, quinone) and 1.96 (br. s, CH₃).
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