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FORMATION AND PHOTOLYSIS OF 1:1 AND 2:1 MOLECULAR COMPLEXES OF MALEIMIDE AND QUINOL

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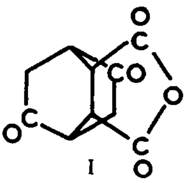
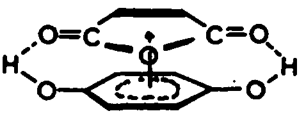
Abstract—Molecular complexes of maleimide and quinol having 1:1 and 2:1 stoicheiometry are described, and structures are proposed. UV irradiation of both complexes in the solid phase and in solution gave cyclobutane-1,2-*anti*-3,4-tetracarboxylic acid bis-imide. Orange complexes were obtained by freezing 1:1 and 2:1 molar melts of N-benzylmaleimide and quinol. Solid complexes of N-2,6-xylylmaleimide and quinol, or of maleimide and quinol dimethyl ether, could not be isolated

The preparation of a 1:1 thermal adduct (I) of quinol and maleic anhydride by Cookson and Wariyar provided the first example of the addition of a dienophile to an isolated benzene nucleus.[1] Pfeiffer and Böttler reported orange melts and solutions of quinol and maleic anhydride,[2] and later workers isolated a 1:1 orange molecular complex which dissociated to its components at about 40° without melting.[3] The bonding in the complex was considered to be principally of charge-transfer character stabilized by a degree of hydrogen bonding between the component molecules: structures II and III were suggested to accommodate these ideas[3] which differ somewhat from current belief on the structure of the formally analogous quinhydrone.[4] A stable, yellow 1:1 complex of resorcinol and maleimide, m.p. 126–128°, has been isolated by Tawney *et al.*[5] The complex exhibited an UV absorption maximum at 329 nm.


I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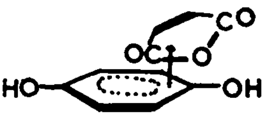

III

A mixture of quinol and maleimide in all common organic solvents is yellow whereas the components are colourless. The position of the new absorption maximum could not be determined, however, due to the intense absorption of the solutes. Slow evaporation of solvent from an ethereal solution of maleimide and quinol gave orange and yellow crystals of 1:1 and 2:1 adducts respectively. These adducts are better prepared by cooling melts of the corresponding compositions. Both compounds had discrete m.ps and readily dissociated to their component molecules under TLC. A melt and solutions of 1,4-dimethoxybenzene and maleimide in organic solvents are pale yellow but no complexes could be isolated. 1,4-Dimethoxybenzene is expected to have similar donor characteristics to quinol but does not possess OH protons which could H-bond with a maleimide molecule and so stabilize the molecular complex.

The IR spectra of the two adducts of quinol and maleimide are shown in Fig. 1. The IR spectra of intimate 1:1 and 2:1 mixtures of maleimide and quinol closely resembled the spectrum of the 2:1 adduct. The main features of Fig. 1 are that the OH protons[6a] at ca. 3320 cm^{-1} and the NH proton[6b, 7] at ca. 3230 cm^{-1} are hydrogen bonded in both adducts. The CO stretching frequency is at 1710 cm^{-1} in the 2:1 adduct but it is shifted to 1695 cm^{-1} in the 1:1 adduct (cf. maleimide, broad band $\bar{\nu}_{max}$ 1700 cm^{-1}). This difference in the IR spectra may be attributed to the CO groups in the latter adduct being the more strongly H-bonded, and/or (as we have been reminded by a referee) the different electrostatic or van der Waals' interactions between neighbouring molecules in the solid state of each adduct. The diffuse reflectance spectra of the two adducts are shown in Fig. 2; there are indications of a maximum at a wavelength shorter than 370 nm in the spectrum of the yellow adduct.

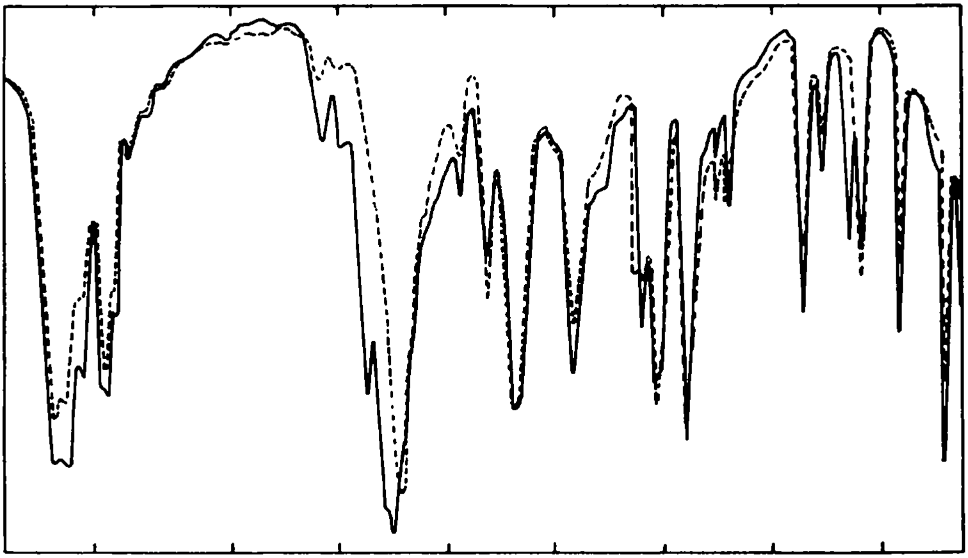


FIG. 1 IR Spectra of 1:1 adduct (-----) and 2:1 adduct (———) of maleimide and quinol (Nujol mulls).

It is concluded from these results that the adducts of maleimide and quinol are best described as molecular complexes in which H-bonding between the component molecules is important for their stabilization. The colour of the complexes is probably due to charge-transfer absorption.

Previous workers[8] have concluded that the stability and stoicheiometry of solid quinhydrone-like complexes is determined by H-bonding. Maleimide may be considered to possess at least four H-bonding centres, *viz.*, the two O atoms, the N atom, and its attached proton. Quinol also has four such centres. If the CO groups in the 1:1 adduct are more H-bonded than in the 2:1 adduct (IR evidence), it seems reasonable to assume that the main bonding in the 1:1 adduct involves these groups. Accordingly each maleimide molecule can only associate with one quinol molecule.[8]

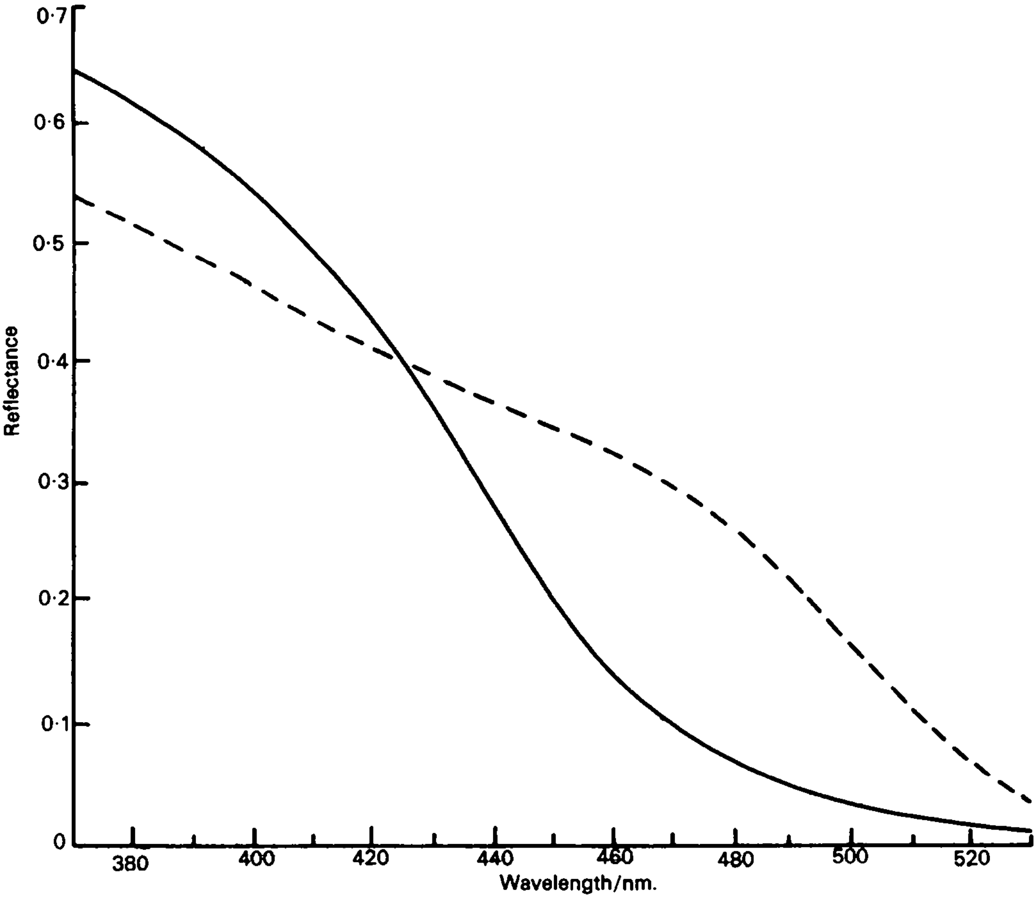


FIG. 2 Diffuse reflectance spectra of 1 : 1 and 2 : 1 adducts of malemide and quinol.
----- 1 : 1 adduct, 34·6 mg/198·4 mg SiO_2.
—— 2 : 1 adduct, 38·9 mg/194·4 mg SiO_2.

Two maleimide molecules can associate *via* their N atoms with one molecule of quinol giving rise to a 2 : 1 adduct. It is proposed that the structures shown in Figs 3 and 4 would accommodate these ideas.

The symmetries of the highest and second highest occupied molecular orbitals of quinol[9] are shown in structures IV and V respectively, and the lowest unoccupied

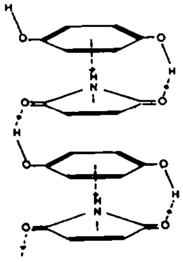


FIG. 3 Suggested structure of 1 : 1 adduct of maleimide and quinol.

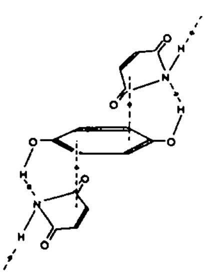
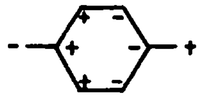
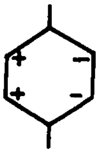


Fig. 4 Suggested structure of 2:1 adduct of maleimide and quinol

MO of maleimide[10] is illustrated in structure VI. A complex of structure shown in Fig. 3 would involve overlap of donor and acceptor orbitals of types IV and VI respectively, and a 2:1 complex (Fig. 4) would involve overlap of orbitals represented by structures V and VI. It can be seen that both orientations are suitable for charge-transfer.



IV



V

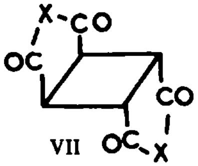
VI

Orange solids having wide, but different, melting ranges were obtained by freezing 1:1 and 2:1 melts of N-benzylmaleimide and quinol. The IR spectra of the solids had identical stretching frequencies but were slightly different from that of an intimate mixture of the imide and quinol. H-bonding of the OH groups was greatly reduced in the orange compounds (OH at 3410 cm^{-1}, cf, 3250 cm^{-1} in the mixture) but the CO absorption band was at the same position in all the IR spectra. It is evident that molecular complexes of unknown stoicheiometry and exhibiting charge-transfer are formed between N-benzylmaleimide and quinol. The weak H-bonding in these complexes is probably due to steric hindrance of the N-benzyl group to close approach of an imide and quinol molecule.

The Me groups in N-2,6-xylylmaleimide are expected to cause steric hindrance coplanarity of the maleimide and aryl rings.[11] It is not surprising, therefore, that isolation of the yellow component of solutions or melts of quinol and this imide was not possible. The large size of the imide molecule probably hinders the close approach of an imide and quinol moiety within a complex and restricts the formation of stabilizing intermolecular H-bonds. Evidence for charge-transfer in this system is provided by the colour of the solutions and melts.

In the light of the present results with maleimide, it is surprising that previous workers obtained only a 1:1 complex from maleic anhydride and quinol.[3] Maleic anhydride and maleimide have approximately the same size and acceptor properties, so the ability of maleimide to form a 2:1 complex probably results from H bonding through its N—H group: see Fig. 4.

Irradiation of the crystalline 2:1 maleimide-quinol complex, or a solution of the components in Me_2CO or MeCN (253·7 nm), gave cyclobutane-1,2-*anti*-3,4-tetracarboxylic acid bis-imide (VII; X = NH), identified by its synthesis from the known corresponding anhydride.[12,*] No trace was detected of a 2:1 photoadduct analogous to that formed from melts of maleic anhydride and quinol.[3]



VII

EXPERIMENTAL

Maleimide and quinol were commercial products and were used without further purification. A sample of 1,4-dimethoxybenzene was kindly supplied by Dr. A. Gilbert. The N-substituted maleimides were prepared as described elsewhere.[11]

UV spectra were measured on solns made up in a spectroscopic grade of EtOH. Solns, 0·1M in the acceptor and 0·05M in quinol, were examined by placing them in separate 1 cm silica cells in the sample beam of the instrument and recording the spectrum; 15 ml of each soln were mixed and the spectrum of the resulting soln was recorded in a matched 2 cm silica cell. The difference between the two spectra, thus obtained, is attributed to charge-transfer absorption. The spectra were obtained on a Perkin–Elmer 137 UV recording spectrophotometer.

The diffuse reflectance spectra of the 1:1 and 2:1 molecular complexes of maleimide and quinol were measured on intimate mixtures of the complexes with silica gel. A silica gel reference was used. The spectra were obtained on a Unicam SP500 manual instrument and are recorded in the text.

Orange and yellow adducts of maleimide and quinol. A soln of quinol (1·13 g, 0·01 moles) and maleimide (0·50 g, 0·005 moles) in Et_2O (50 ml) was allowed to evaporate slowly at room temp. A mixture of orange, yellow and white solids was obtained from which small amounts of each could be obtained in a reasonably pure state by hand-picking. The white solid was identified as quinol (m.p., mixed m.p.). The yellow and orange products melted at 129–131·5° and at 130–167°, respectively.

The orange product, which was obtained in the largest amounts, was dissolved in Me_2CO. Addition of CCl_4 to the soln precipitated a mixture of yellow and white crystals which were easily separated by hand-picking. The white crystals were of quinol (m.p., mixed m.p., IR spectrum). The yellow solid had m.p. 133·5–135°. (Found: C, 55·75; H, 3·98; N, 9·02. $C_{14}H_{12}N_2O_6$ requires: C, 55·27; H, 3·97; N, 9·21%). The IR spectra of the orange and yellow products are recorded in the text (Fig. 1).

The same results were obtained with a 1:1 molar mixture.

Yellow 2:1 adduct of maleimide and quinol. Maleimide (1 g, 0·01 moles) and quinol (1·1 g, 0·01 moles) were dissolved in hot Me_2CO (8 ml). On cooling, the solution deposited yellow crystals (0·22 g) which were filtered off and recrystallized from Me_2CO to give bright yellow tablets, m.p. 133–134·5°. (Found: C, 55·40; H, 3·93; N, 9·40. $C_{14}H_{12}N_2O_6$ requires: C, 55·27; H, 3·97; N, 9·21%). The IR spectrum of the complex is recorded in the text (Fig. 1).

Crystallization of 1:1 and 2:1 molar melts or maleimide and quinol. 1:1 and 2:1 Molar mixtures of maleimide and quinol were ground together. The mixtures which became yellow in colour were then melted quickly in a shallow container over a bunsen flame to give orange melts which were allowed to cool. The 1:1 molar mixture yielded orange crystals m.p. 126·5–130°. The IR spectrum is recorded in the text (Fig. 1). Bright yellow crystals m.p. 131–133·5° were obtained from the 2:1 molar mixture. The IR spectrum is recorded in the text (Fig. 1).

IR spectrum of an intimate 1:1 molar mixture of maleimide and quinol. $\bar{\nu}_{max}$ (Nujol mull) 3320, 3220, 3100 (s), 1835 (w), 1755 (m), 1710 (s), 1585, 1530 (w), 1240, 1215 (m), 1155 (s), 1095, 1074, 1065 (w), 940 (m), 905 (w), 852, 836, 760 (m), 680 (s) cm^{-1}.

Thin layer chromatography of the 1:1 and 2:1 complexes of maleimide and quinol. TLC plates were coated with silica gel (Whatman, SG41). The compounds were eluted with 5% EtOH in $CHCl_3$ and sprayed with a 5% phosphomolybdic acid soln in Pr^iOH, heated at 115° for 10 min and developed in an ammonia jar.

Both complexes gave two spots identified as quinol and maleimide. Quinol and maleimide have R_f values of 0·43 and 0·78 respectively under these conditions.

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[*] Me_2CO was used as solvent in place of dioxan for preparation of the anhydride.

Crystallization of 1:1 *and* 2:1 *molar melts of* N-*benzylmaleimide and quinol.* The procedure was the same as that described for the maleimide case.

The orange solid from the 1:1 molar melt of N-benzylmaleimide and quinol melted at 71·3° to an orange liquidus layer and a white solid which finally melted at 131·5°.

The orange 2:1 product melted at 66° to a liquidus layer and a white solid which finally melted at 106°.

IR spectra of both products were identical save for slight differences in the relative intensities of a few peaks: $\bar{\nu}_{max}$ (Nujol mull), 3410 (s), 3110, 1760 (m), 1700 (s), 1603, 1585 (w), 1430 (m), 1473, 1445 (s), 1412 (m–s), 1395 (m), 1365, 1350 (m–s), 1310 (m), 1290 (w), 1255 (m), 1215 (m–s), 1163 (w), 1145, 1103 (m), 1080 (w–m), 1030 (w), 883, 845 (w–m), 830 (m–s), 785 (w), 760, 728 (m), 695 (s) cm^{-1}.

Solid molecular complexes of 1,4-dimethoxybenzene and maleimide and quinol and N-2,6-xylylmaleimide could not be isolated by evaporation of the solvent from a soln or by crystallization of 1:1 and 2:1 molar melts of the compounds. In each case a colourless mixture of the two components was obtained.

The UV irradiation of a solution of maleimide and quinol in Me_2CO

Method I. A soln of maleimide (2 g) and quinol (1 g) in Me_2CO or MeCN (40 ml) was contained in a fused quartz thimble which was suspended in a spiral Hanovia 15-W low-press Hg vapour lamp. The quartz thimble was flushed with N_2 and sealed. This soln was irradiated for 50 hr at room temp. At the end of each 5-hr period the precipitated solid was filtered from the soln. A total of 145 mg of a cream solid was obtained. The soln was dark yellow and smelt strongly of biacetyl; the only solid compounds isolated from this soln were maleimide and quinol.

The solid product (145 mg) was insoluble in hot and cold Et_2O, $CHCl_3$, Me_2CO, EtOH, glacial HOAc and dioxan. It was soluble in Me_2SO and $HCONMe_2$ but could not be precipitated in a pure form by addition of other solvents to either soln. The product could not be vacuum sublimed successfully.

The product was purified by heating it with $HCONMe_2$ (10 ml) for a few min and filtering off the undissolved solid from the brown soln; the residue was washed with a large quantity of Me_2CO and dried. A white solid residue was obtained which did not melt at 400° but began to darken in colour at 300°. [Found: C, 49·45; H, 3·09; N, 14·32. $(C_4H_3NO_2)_n$ requires: C, 49·49; H, 3·11; N, 14·43%]. The NMR spectrum of a sat soln in $(CD_3)_2SO$ showed only one signal at τ 6·70; $\bar{\nu}_{max}$ (Nujol mull) 3175, 3100 (m), 1765, 1708 (s), 1468, 1420 (w), 1360 (s), 1305 (m), 1210, 1200, 1170 (s), 1000 (m), 910 (w), 870, 838, 748 (m) cm^{-1}.

Method II. A soln of maleimide (2 g) and quinol (1 g) in Me_2CO (50 ml) was contained in a borosilicate glass flask and irradiated, in an atmosphere of N_2, with the light from an Hanovia S500 medium press, Hg vapour lamp for 55 hr. The soln was magnetically stirred and the flask was periodically turned during the reaction. The soln soon darkened and a buff-coloured solid was precipitated. This product (75 mg) had an IR spectrum identical with that of the product described above. Unused starting materials were retrieved from the soln.

Irradiation of the 2:1 *complex of maleimide and quinol.* The 2:1 complex of maleimide and quinol (1·6 g) was cast (from the melt) as a film on the inside of a 100 ml borosilicate glass flask. The film was rotated in front of a 125-W medium press Hg vapour lamp for 33 hr. The solid was digested with Me_2CO and filtered. A buff solid (5 mg) was obtained and was identified as the photodimer of maleimide (IR spectrum).

Conversion of the maleic anhydride dimer to the tetramethyl ester. Conc. H_2SO_4 (1 drop) was added to a soln of the maleic anhydride dimer[12] (0·3 g) in MeOH (10 ml) and the whole was refluxed for 4 hr. Upon cooling, crystals of tetramethyl-*cis,trans,cis*-cyclobutane-1,2,3,4-tetracarboxylate separated. The product (0·38 g) was recrystallized from MeOH, m.p. 144·5–145° (Lit.[13] 145°). (Found: C, 49·95; H, 5·47. Calculated for $C_{12}H_{16}O_8$ C, 50·0; H, 5·60%); NMR spectrum in $CDCl_3$ τ 6·22 (1H), 6·28 (3H).

Conversion of the maleic anhydride dimer (VII; X = O) *into the corresponding bis-imide* (VII; N = NH). A melt of the maleic anhydride dimer (0·3 g)[12] and urea (2 g) was maintained at 140° for 2·5 hr. The cooled melt was extracted with boiling water (20 ml), filtered hot and the residue washed with Me_2CO. The product (80 mg) did not melt below 400° and had IR and NMR spectra identical with those of the maleimide dimer prepared photochemically.

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