

The Ultra-Violet Absorption Spectra of Some Derivatives of Naphthols.

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Accounts¹ have already been given of the catalytic hydrogenation of α - and β -naphthols and their methyl ethers with respect to the effect of added atomic groups such as hydroxyl and methoxyl groups to the naphthalene molecule, and also to that of the spatial disposition of these groups.

The absorption spectra of naphthalene and its hydroxyl, halogen and nitro derivatives have been described by W. N. Hartley, by E. C. C. Baly and W. B. Tuck, and by J. E. Purvis.² Baly and Tuck have proposed a constitutional formula for naphthalene, from the comparison of the absorption spectra of naphthalene with those of dihydro- and tetrahydronaphthalenes.

The present investigation, in connection with our previous researches, was undertaken to examine how the absorption spectra of naphthalene would be affected by the added atomic groups, and also by the position in which they attached themselves to the naphthalene ring.

The substances, the authors have examined in their alcoholic solution, were the α - and β -naphthols, the α - and β -naphthyl methyl ethers and their ar-tetrahydro compounds. The methods of observation were as usual; the source of light was the iron spark, and the photographs were taken with the Féry spectrograph from Adam Hilger. The curves were plotted from the photographs in the usual way.

¹ S. Komatsu and R. Nodzu: These Memoirs, **6**, 177 (1923); S. Komatsu and S. Kumamoto: Ibid., **7**, (1923).

² W. N. Hartley: J. Chem. Soc., **87**, 685 (1885); J. E. Purvis: Ibid., **101**, 1315 (1912); E. C. C. Baly and W. B. Tuck: Ibid., **93**, 1902 (1908).

α- and β-Naphthols and α- and β-Tetrahydronaphthols.

α-naphthol shows four bands, namely, three narrow ones at 3100, 3200 and 3750, and a broad band with its head at about 3500, and *β*-isomer three bands, two narrow ones at about 3000 and 3250, and a broad one with the head at 3700. (Fig. 5) Their absorption curves differ from those described by Purvis of the same compounds; there are in our case two more bands in *α*-compound and one more in *β*-one. When the absorption curves of naphthalene studied by Baly and Tuck¹ are compared with those of the naphthols, there is a general resemblance between these absorption curves, but there are some differences with respect to the position of the head and the form of the broad band as seen in Fig. 1, in the latter compounds the head is divided into two (in *α* only) and they are all shifted toward the visible region of spectra, and moreover, with respect to the intensity of absorption, namely, the narrow bands of naphthalene were affected hyperchromically by the introduction of the hydroxyl group in the molecule. When, however, compared with each other (*α* and *β*) the bands are widened out in the *β*-derivative, as noticed by Purvis².

In the hydrogenated compounds, showing three bands (3200, 3500 and 3700) in the *α*-compound, and four bands (3000, 3200, 3500 and 3700) in the *β*-isomer. By the introduction of hydrogen, the heads of the broad bands of naphthols are again shifted back to the ultra-violet regions of spectra, and the intensity of the narrow bands were lessened. The absorption curves of both isomers are quite similar to each other (Fig. 7), and moreover they resemble those of the naphthalene (Figs. 1, 3 and 5).

α- and β-Naphthyl Methyl Ethers and α- and β-ar-Tetrahydronaphthyl Methyl Ethers.

When the H atom of the OH group of naphthols was replaced by the methyl group, the absorption bands were increased; in the *α*-

¹ Loc. cit.

² Loc. cit.

compound from 4 bands to 5 (3150, 3250, 3450, 3550, and 3800), and analogously in the β -one, from 3 bands to 4 (3050, 3200, 3550 and 3740).

The general forms of the absorption curves of α - and β -naphthyl ethers, however, show no marked difference from those of the corresponding naphthols (α and β). The only difference to be noticed when comparing α -naphthyl methyl ether with α -naphthol, is that the broad band of the latter with the head at 3460 is divided into two in the former, and a similar relation is also held in the case of the β -isomers, as will be seen in Figs. 5 and 6.

In hydrogenated methyl ethers, there are three absorption bands in the α -compound, but four in the β -isomer; the number of bands in the α -compounds decreased from five to four by the hydrogenation, while in the β -isomers remaining constant. Such a relationship in the number of the absorption bands will be noticed in comparing naphthols with their hydrogenated compounds.

Consequently, the number of absorption bands and the form of the curves of α -naphthol are more like those of the α -naphthyl methyl ether than those of the β -naphthol, and the similarity is held among their hydrogenated compounds in this respect.

The addition of hydrogen to the non-substituted benzenoid nucleus of the naphthol molecule, exerts an influence on the absorption of the compounds to produce a hypochromic effect, especially on the position near to the visible region of the spectra.

SUMMARY.

1. The introduction of the hydroxyl group into naphthalene, converting it into α - and β -naphthols, was effected to break up the broader absorption band of naphthalene into two in the α -compound, and the origin of this band Baly and Tuck have attributed to the benzenoid portion of the naphthalene molecule.
2. The hydroxyl group has a hyperchromic and bathochromic effect on the absorption of naphthalene, and the bathochromic effect of this group on the broader absorption band was markedly in the α -compound.

3. By replacing the hydrogen atom of the hydroxyl group with the methyl group, there is no marked difference on the absorption curves of the naphthols and their derivatives, and the same relation has already been noticed by Hartley¹ in phloroglucinol and its trimethyl ether and by Baly and his co-operators² in phenol and anisol, and other compounds. Consequently, the authors may suggest that differences in the nature and type of the absorption bands of naphthalene, its hydroxyl and methoxyl derivatives, are mainly due to the introduction of new linking -C-O- into the naphthalene molecule.
4. When naphthols are partially hydrogenated so as to become ar-tetrahydronaphthols, there appears again the hypochromic effect on the narrow bands of the naphthols, and a hypsochromic one on the broad bands, and the latter effect was especially noticeable in the α -compounds.
5. The narrow absorption bands of α -naphthyl methyl ether were so affected as to reduce from two to one by the partial hydrogenation to the non-substituted benzene nucleus of the naphthalene derivatives.
6. The effect of the added hydroxyl group and of hydrogen atoms on both the narrow and broad absorption bands of naphthalene are much more noticeable in the α -compounds than in the β -isomers.
7. The difference between the absorption curves of α - and β -compounds should be attributed to the spatial disposition of the substituted groups in the naphthalene molecule, namely, to the symmetry of the molecular structure.

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¹ W.N.Hartley : J. Chem. Soc., **81**, 936 (1902).

² E. C. C. Baly : J. Chem. Soc., **85**, 1347 (1904) ; **87**, 1332 (1905).

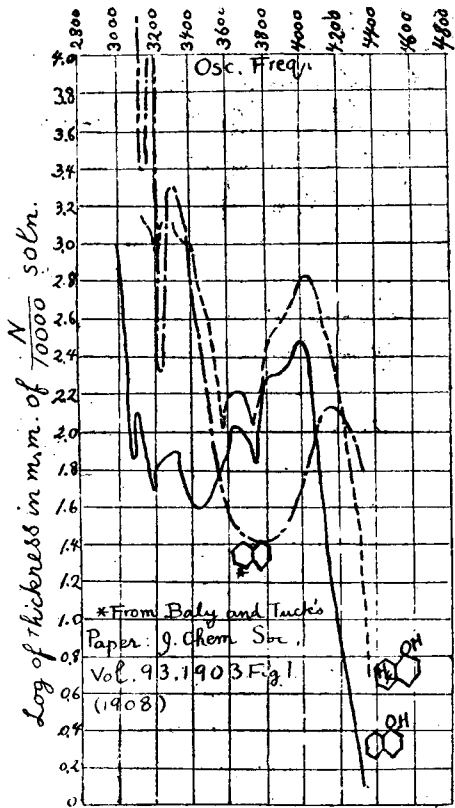


Fig. 1.

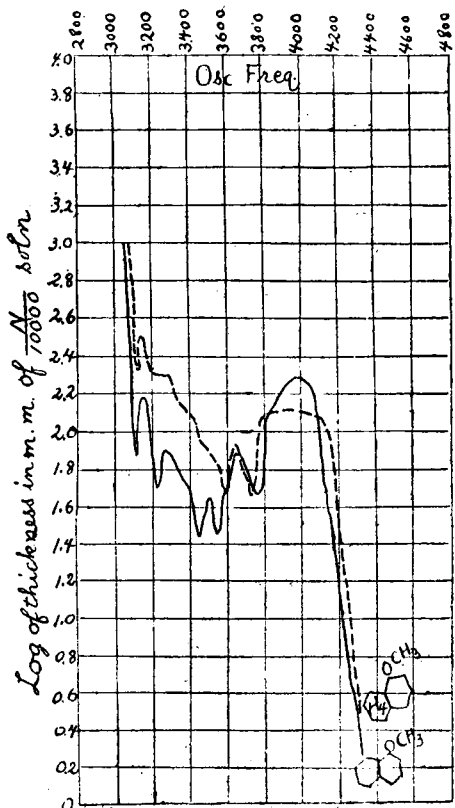


Fig. 2.

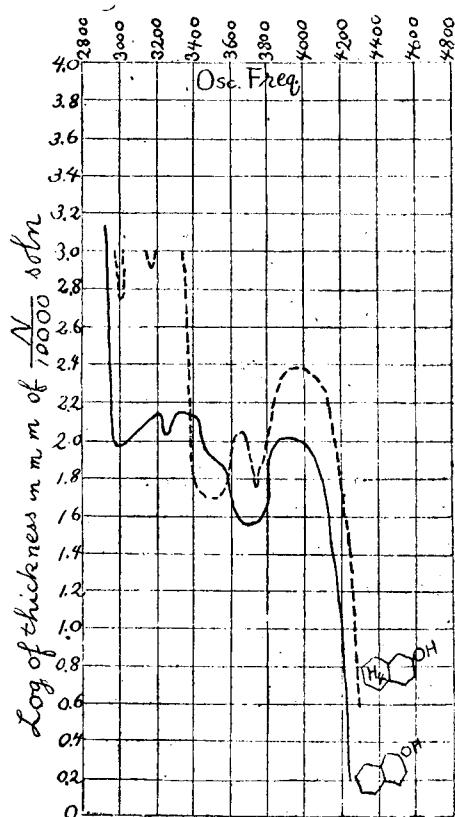


Fig. 3.

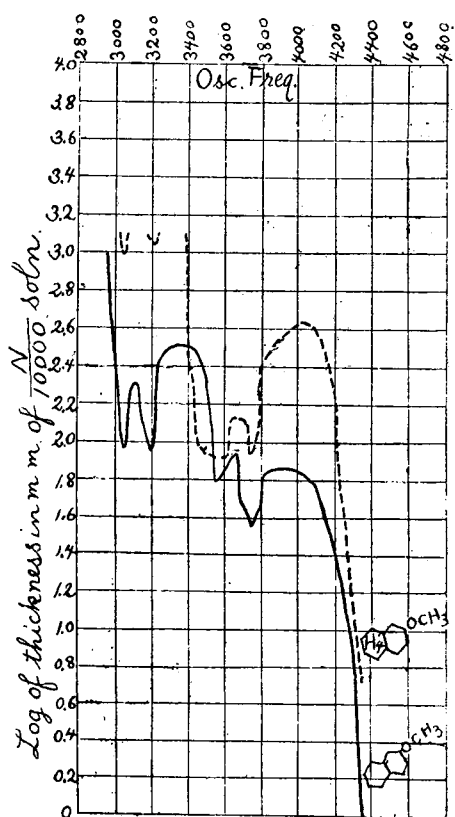


Fig. 4.

