[Contribution from the Baker Chemical and the Rockefeller Physical Laboratories of Cornell University]

THE ABSORPTION SPECTRA OF DI- AND TRIPHENYLMETHANE, THEIR CARBINOLS AND TRIPHENYLMETHYL CHLORIDE[1]

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Received December 27, 1926 Published June 7, 1927

In connection with our research on the absorption spectra of dyes and other related compounds of the triphenylmethane series[4] and in view of the lack of completely reliable data in the literature, it was found desirable to determine the ultraviolet absorption of diphenylmethane, diphenyl carbinol, triphenylmethane, triphenyl carbinol and triphenylmethyl chloride.

Although the absorption of diphenylmethane has been studied by a number of investigators,[5] the recorded data are not only conflicting but are lacking in the finer detail which our improved technique has enabled us to uncover. The sample of diphenylmethane used in this investigation was prepared by Dr. Snow,[6] by the condensation of benzene and benzyl chloride in the presence of mercuric chloride and aluminum.[7] It was purified by repeated distillation and crystallization, the final product having a melting point of 26–27° and boiling point of 257–257.5°. Nevertheless, the product still contained a trace of anthracene, as is evident from the absorption spectrum (Fig. 1, Curve A'). The group of bands between frequency numbers 2600 and 3300, which are drawn in with a broken line, have exactly the positions and relative intensities reported by Hyatt[8] and others for anthracene. A calculation from the absorption coefficients shows that our sample contained 0.025% of anthracene. Because of the low concentrations of diphenylmethane used in determining its absorption in the further ultraviolet region, this small amount of anthracene could not produce an appreciable effect on the intensity of absorption.

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[1] The assistance of a grant made to the first two authors from the Heckscher Research Foundation of Cornell University which enabled us to make the measurements described in this report is gratefully acknowledged.

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[4] Orndorff, Gibbs and McNulty, This Journal, **47**, 2767 (1925). Orndorff, Gibbs and Shapiro, *ibid.*, **48**, 1327, 1994 (1926).

[5] (a) Baker, *J. Chem. Soc.*, **91**, 1490 (1907). (b) Purvis and McCleland, *ibid.*, **101**, 1514 (1912). (c) Purvis, *ibid.*, **105**, 590 (1914). (d) Baly and Tryhorn, *ibid.*, **107**, 1058 (1915). (e) Massol and Faucon, *Compt. rend.*, **166**, 819 (1918).

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[7] Radziewanowski, *Ber.*, **27**, 3235 (1894); **28**, 1135 (1895).

[8] (a) Hyatt, *Phys. Rev.*, **19**, 391 (1922). (b) Marchlewski and Moroz, *Bull. soc. chim.*, **33**, 1405 (1923). (c) Capper and Marsh, *J. Chem. Soc.*, **129**, 724 (1926).

In the further ultraviolet region, Curve *A*, there are three prominent bands at 3712, 3814 and 3942 with a less pronounced band at 3845 and shoulders at 3765, 4009 and 4112. In the complexity of its spectrum diphenylmethane is similar to benzene, although it shows a much greater intensity of absorption.

Diphenyl carbinol (benzohydrol) was prepared by means of the Grignard reagent from benzaldehyde and bromobenzene. It was recrystallized twice from alcohol and had a melting point of 67–68°. Its absorption, Curve *B*, shows no bands in the near ultraviolet, a further corroboration that the bands in that region in diphenylmethane are due to anthracene, since it cannot occur as a by-product in this synthesis of diphenyl carbinol. In the region beyond frequency number 3600, the absorption curve runs fairly parallel to that of diphenylmethane. The bands are located at 3723, 3773, 3818, 3860, 3954, 4040 and 4130, being displaced somewhat toward the further ultraviolet with respect to the corresponding bands in diphenylmethane.

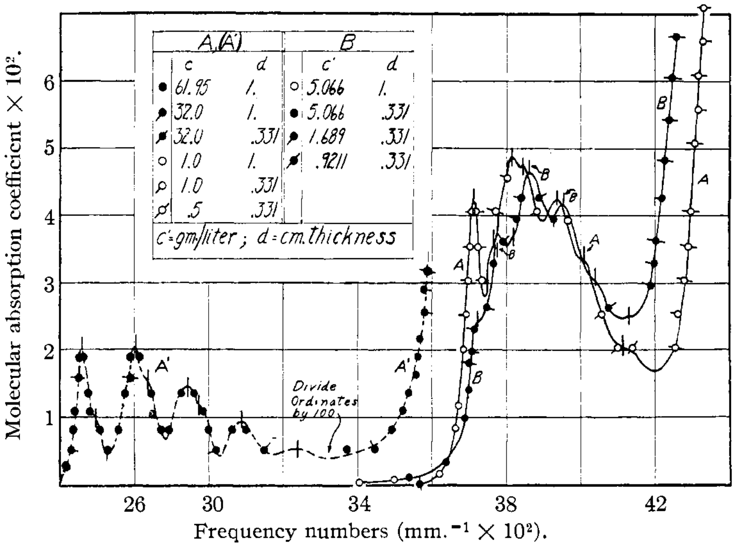

Fig. 1.—Neutral absolute alcohol solution. *A*, diphenylmethane; (*A'*), due to the presence of 0.025% of anthracene in the sample of diphenylmethane; *B*, diphenyl carbinol (benzohydrol).

Although triphenylmethane, its carbinol and chloride have been investigated by several observers,[5a,5e,9] only broad bands are recorded without any indication of a fine structure such as we find.

Fig. 2 shows the absorption spectra of neutral alcoholic solutions of triphenylmethane, triphenylmethyl chloride and triphenyl carbinol.

[9] (a) Hartley, *J. Chem. Soc.*, **51**, 152 (1887). (b) Hantzsch, *Ber.*, **52**, 509 (1919).

Triphenyl carbinol was prepared by means of the Grignard reagent from purified benzophenone and bromobenzene, and after two crystallizations from alcohol it had a melting point of 160–161°. Triphenylmethyl chloride was obtained from triphenyl carbinol by the action of acetyl chloride, and after recrystallization from dry benzene and petroleum ether it gave a melting point of 109–110°. In order to avoid contamination of the triphenylmethane by anthracene it was prepared by the reduction of triphenylmethyl chloride under the action of sulfuric acid and ethyl alcohol.[10] It was purified by distillation, the fraction boiling between 354 and 355° being saved and recrystallized from alcohol; m. p., 92.5–93°. The presence of four weak bands in the near ultraviolet region, Curve A', led us to recrystallize it from ethyl alcohol, thus reducing the intensity of these bands to about one-sixth, without changing the characteristic bands in the further ultraviolet region. As these bands do not appear in the absorption spectra of triphenyl carbinol or triphenylmethyl chloride, the presence of an impurity not greater than 0.03% is probably due to the further action of alcohol and concd. sulfuric acid on the triphenylmethyl chloride. The absorption, Curve A, characteristic of triphenylmethane proper, is marked by two prominent bands at 3708 and 3813, with eight weak bands at 3738, 3766, 3832, 3861, 3908, 3933, 4006 and 4106. The intensity of absorption is much greater throughout than in the case of diphenylmethane, although there is a fairly close correspondence in the position of the bands in these two substances. (See Fig. 9 in succeeding article.) In general, in passing from benzene

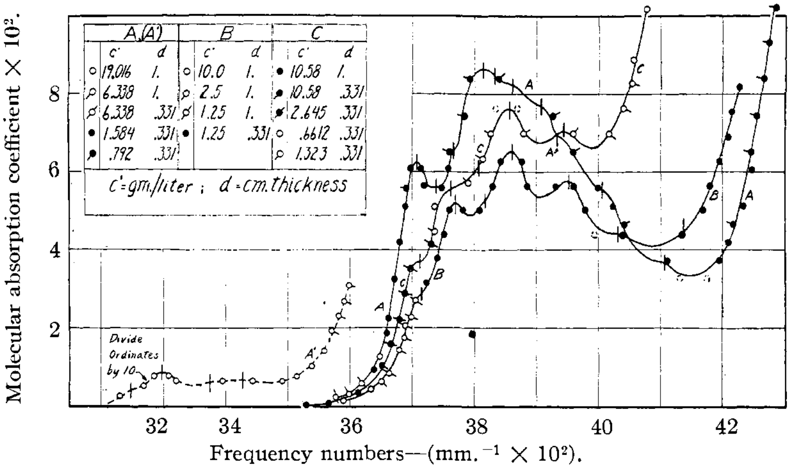

Fig. 2.—Neutral absolute alcohol solution. A, triphenylmethane; (A'), due to presence of 0.03–0.04% unknown impurity in sample of triphenylmethane; B, triphenyl carbinol; C, triphenylmethyl chloride.

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[10] Schmidlin and Garcia-Banus, *Ber.*, **45**, 3189 (1912).

to diphenylmethane and then to triphenylmethane, the general absorption steadily increases while the bands become less and less pronounced.

Triphenyl carbinol gives an absorption, Curve *B*, that runs fairly parallel to that of triphenylmethane, with an intensity that is somewhat less, except in the extreme ultraviolet region. The bands, located at 3715, 3770, 3817, 3861, 3952, 4031 and 4137, are shifted toward the shorter wave lengths as compared to those for triphenylmethane. This phenomenon, which occurred also in the case of diphenylmethane and diphenyl carbinol, is somewhat unusual, as the effect of increasing the molecular weight of a compound is ordinarily to force the absorption bands toward longer wave lengths.

The absorption of triphenylmethyl chloride is shown on Curve *C* and is quite similar to that of triphenyl carbinol with the bands at 3712, 3762, 3807, 3857 and 3944 shifted, in the normal manner, toward lower frequencies. The intensities of the bands are intermediate between those of triphenylmethane and triphenyl carbinol, except in the extreme ultraviolet region. Here, apparently, the presence of the chlorine atom is responsible for a sharp rise in the absorption, with the obliteration of the two weak bands found in triphenylmethane and triphenyl carbinol at about 4000 and 4100.

The absorption of triphenyl carbinol in concd. sulfuric acid solution is described in the succeeding article[11] together with that of fuchsone and aurin in the same solvent.

Table I gives the frequency numbers of the bands found in di- and triphenylmethane and some of their derivatives.

TABLE I

FREQUENCY NUMBERS OF BANDS IN ALCOHOLIC SOLUTIONS

Diphenyl-methane	Diphenyl carbinol	Triphenyl-methane	Triphenyl carbinol	Triphenyl-methyl chloride
3712	3723	3708	3715	3712
		3738		
3765	3773	3766	3770	3762
3814	3818	3813	3817	3807
		3832		
3845	3860	3861	3861	3857
		3908		
3942	3954	3933	3952	3944
4009	4040	4006	4031	
4112	4130	4106	4137	

(Note added in proof, May 21, 1927.) Since the above article was submitted for publication, a paper by Castille has appeared in *Bull. acad. roy. Belg.*, [v] **12,** 498 (1926), giving data on the absorption of diphenylmethane

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[11] Orndorff, Gibbs, McNulty and Shapiro, THIS JOURNAL, **49**, 1545 (1927).

in hexane solution, which agrees substantially with our results for an alcoholic solution.

Summary

1. The absorption curves of diphenylmethane and diphenyl carbinol, and of triphenylmethane, triphenyl carbinol and triphenylmethyl chloride in neutral absolute alcohol solution have been determined and their relations discussed.

2. A table has been prepared, showing the frequency numbers of the peaks of the absorption bands of the various substances studied.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE BAKER CHEMICAL AND ROCKEFELLER PHYSICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF FUCHSONE, BENZAURIN AND AURIN[1]

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RECEIVED DECEMBER 27, 1926 PUBLISHED JUNE 7, 1927

In continuation of our work on the absorption spectra of triphenylmethane derivatives,[4] we are reporting now on fuchsone, *p*-hydroxytriphenyl carbinol and aurin, together with some further data on benzaurin.[4a] Fuchsone has been investigated by Meyer and Fischer,[5] who found two bands in its neutral alcoholic solution at frequency numbers (estimated from their curves) 2630 and 3850. Schlenk and Marcus[6] and Hantzsch[7] each located but one band in the neighborhood of 2600. Aurin has been studied by Hartley,[8] whose data indicate three bands at 2640, 2800 and 3700 in the neutral solution. However, none of these investigators have made any study of the fading of neutral alcoholic solutions of fuchsone and aurin which have been allowed to stand for some time in the dark. Ghosh and Watson[9] have reported two bands in the visible region at frequency numbers 1830 and 2000 for an alkaline solution of aurin.

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[4] (a) Orndorff and co workers, THIS JOURNAL, **47**, 2767 (1925); (b) **48**, 1327; (c) 1994 (1926); (d) **49**, 1541 (1927).

[5] Meyer and Fischer, *Ber.*, **46**, 70 (1913).

[6] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

[7] Hantzsch, *Ber.*, **52**, 509 (1919).

[8] Hartley, *J. Chem. Soc.*, **51**, 152 (1887).

[9] Ghosh and Watson, *ibid.*, **111**, 815 (1917).