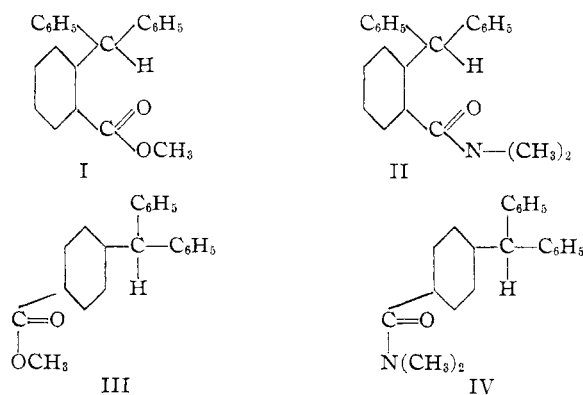


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Hydrogen Bonds Involving the C-H Link. XV.¹ Non-Bonding of Triphenylmethane Hydrogen Atoms

BY C. S. MARVEL AND JAMES HARKEMA

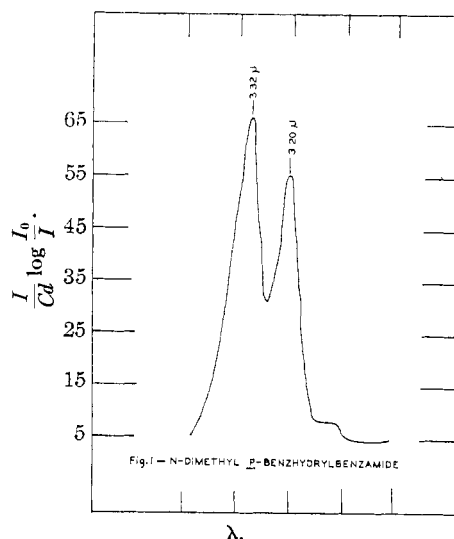
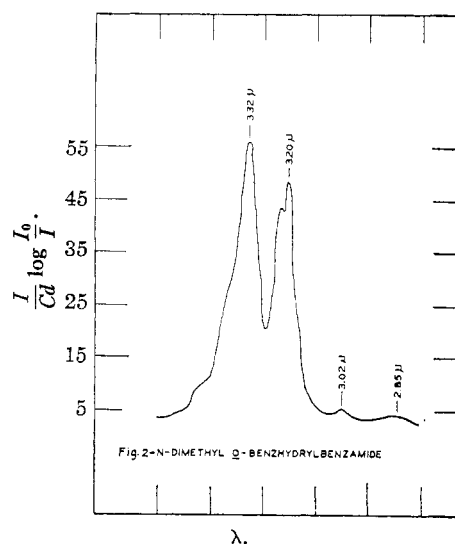
Many cases of hydrogen bonding of a C-H group have been reported but none of these involves the formation of a chelate ring. The methyl ester (I) and the N,N-dimethylamide (II) of *o*-benzhydrylbenzoic acid seemed to be compounds in which this type of chelation might occur. They have been prepared and compared with the corresponding *para*-isomers (III and IV) which might be expected to associate if the hydrogen of a triphenylmethane molecule is active



enough to bond with a donor group. Molecular weight determinations in benzene showed that the compounds were not associated. Infrared absorption spectra in carbon tetrachloride solution showed that hydrogen bonding had not occurred in these molecules as there was no absorption in the 3μ region (see Figs. 1-4). The bands at 3.2 and 3.3μ , respectively, are the aromatic and aliphatic C-H frequencies.²

Experimental

***o*-Benzhydrylbenzoyl Chloride.**—*o*-Benzhydrylbenzoic acid was prepared by the method of Baeyer³ and esterified by the procedure of Jones and Root.⁴ Attempts to follow their directions for the preparation of the acid chloride led to the formation of 9-phenyl-9-chloroanthrone. However, by treating the acid with thionyl chloride at room temperature and removing the excess by passing a stream of dry

Fig. 1.—N-Dimethyl *o*-benzhydrylbenzamide.Fig. 2.—N-Dimethyl *o*-benzhydrylbenzamide.

nitrogen through the reaction mixture, the acid chloride melting at 84° was obtained.

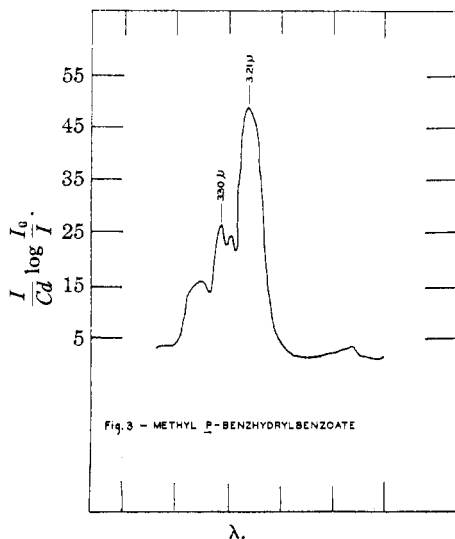
N,N-Dimethyl-*o*-benzhydrylbenzamide.—The acid chloride from 10 g. of the acid was dissolved in ether and dry dimethylamine in excess was passed into the solution. The dimethylammonium chloride was filtered off and the ether evaporated. The amide was crystallized from a mixture of high boiling petroleum ether and benzene. The yield was 8 g. (77%) of a product, m. p. 146° .

(1) For the fourteenth communication see THIS JOURNAL, 63, 1609 (1941).

(2) We are greatly indebted to Mr. M. M. Sparks for making the infrared measurements and to Professors W. H. Rodebush and A. M. Buswell for their interpretation.

(3) Baeyer, *Ann.*, 202, 50 (1880).

(4) Jones and Root, THIS JOURNAL, 48, 190 (1926).

Fig. 3.—Methyl *p*-benzhydrylbenzoate.

*Anal.*⁵ Calcd. for $C_{22}H_{21}ON$: C, 83.81; H, 6.66; N, 4.44. Found: C, 83.68; H, 6.70; N, 4.33.

Methyl *p*-Benzhydrylbenzoate.—*p*-Benzhydrylbenzoic acid was prepared by the method of Staudinger and Clar.⁶ Direct esterification with methyl alcohol in the presence of a little hydrogen chloride gave an 83% yield of the methyl ester, m. p. 78–79°. Schlenk and Bergmann⁷ have prepared this ester from the acid and diazomethane and reported the melting point at 77°.

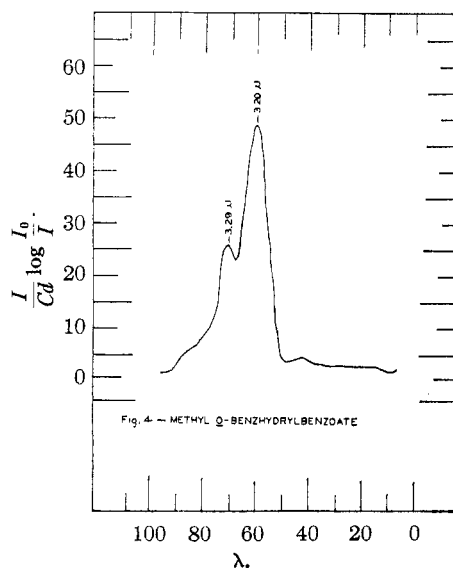
N,N-Dimethyl-*p*-benzhydrylbenzamide.—A mixture of 27 g. of *p*-benzhydrylbenzoic acid and 48 g. of thionyl chloride was heated for one hour and the excess thionyl chloride was removed by distillation under reduced pressure. The residual acid chloride was dissolved in ether and dry dimethylamine was passed into the solution until a slight excess was present. The dimethylammonium chloride was filtered off and the ether distilled. The amide was recrystallized from a mixture of high boiling petroleum ether and benzene. The yield was 19 g. (66%) of a product, m. p. 89–90°.

Anal. Calcd. for $C_{22}H_{21}ON$: C, 83.81; H, 6.66; N, 4.44. Found: C, 83.99; H, 6.83; N, 4.46.

(5) The microanalyses in this paper were carried out by Mr. L. G. Fauble and Miss Mary S. Kreger.

(6) Staudinger and Clar, *Ber.*, **44**, 1623 (1911).

(7) Schlenk and Bergmann, *Ann.*, **480**, 183 (1930).

Fig. 4.—Methyl *o*-benzhydrylbenzoate.

Molecular Weight Determinations.—The molecular weights of the two esters and the two amides in dry, redistilled, thiophene-free benzene were determined by the cryoscopic method over the concentration range of 0.6 g. to 9.6 g. of substance to 100 g. of benzene for each compound. The molal depression constant for benzene (5.1) which was used in the calculations is that given by Peterson and Rodebush.⁸ All of the molecular weight determinations checked within the experimental error for the calculated values.

Infrared Absorption Spectra.—The infrared absorption spectra of the *para* ester and two amides were taken on 0.01 and 0.04 molar solutions in carbon tetrachloride. The *ortho* ester was examined only at 0.01 molar concentration. The four curves are given in Figs. 1–4.

Summary

Evidence has been presented that a triphenylmethane hydrogen atom does not bond with an ester or amide group.

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RECEIVED JUNE 13, 1941

(8) Peterson and Rodebush, *J. Phys. Chem.*, **32**, 709 (1928).