[CONTRIBUTION FROM THE COLLEGE OF PHARMACY AND THE SPECTROGRAPHIC LABORATORY OF THE UNIVERSITY OF CALIFORNIA, SAN FRANCISCO]

The Ultraviolet Absorption Spectra of α-Phenylcarbonyl Compounds[1]

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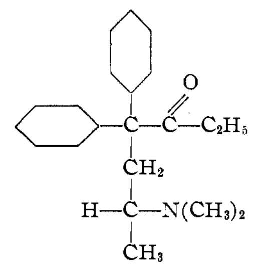
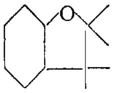
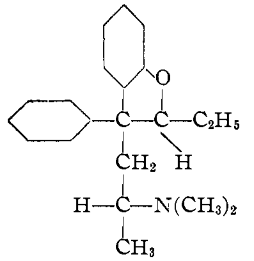
A commonly used and accepted hypothesis in absorption spectroscopy is that two chromophores separated by one or more saturated carbon atoms will absorb independently and the absorption of the compound will be the sum of the absorption of the individual chromophores. Applying this to methadon the compound should have the absorption of diphenylmethane plus that of a ketone, *i. e.*, a band at 260 mμ with an extinction coefficient of about 350 and another band at about 290 mμ with an extinction coefficient of 15–25. Figure 1 shows the compound has a band at 295 mμ with an extinction coefficient of 460 which is most unexpected.



This appears to be explicable only in terms of some type of interaction between the carbonyl and the phenyl groups. One way in which such an interaction could come about would be for the oxygen to be bonded to the ring producing a derivative of coumaran. This could have such an absorption since alkyl coumarans have bands in the 290 mμ region with extinction coefficients of 1500–2200.[2] The dipole moment of the compound was measured to test this rather unlikely possibility. Methadon was found to have a dipole moment of 3.03D which is consistent with a ketone structure and not with a coumaran structure since the former would be expected to have a moment between 2.5 and 3.5 and the latter a moment between 1.0 and 2.0.





Some simple phenyl substituted aldehydes and ketones were next investigated to see if any of them had extinctions around 290 mμ of the order of magnitude of 400. Although the spectra of some of these compounds were in the literature[3–7] it appeared essential that they be remeasured in the same solvent with a modern instrument. In several cases it was found that compounds whose reported spectra showed no fine structure actually had pronounced fine structure. In another case a compound with a reported extinction coefficient of about 1200 at 290 mμ was found to have an extinction coefficient of only 500 when carefully purified.

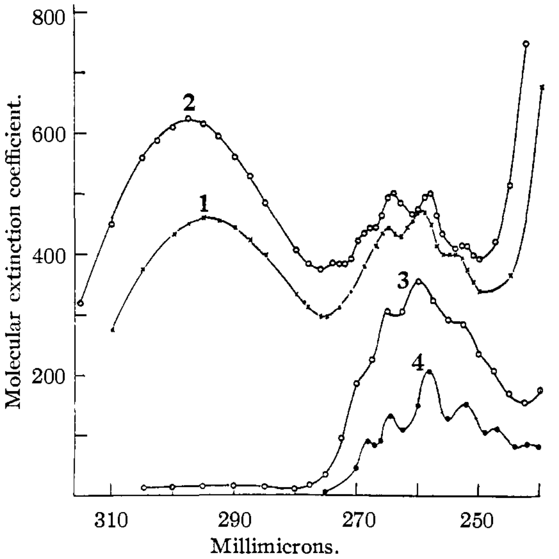


Fig. 1.—Ultraviolet absorption spectra of 1, methadon hydrochloride; 2, isomethadon hydrochloride monohydrate; 3, methadon carbinol hydrochloride; all in 95% ethanol; 4, N-methyl-phenylacetamide in methanol.

The spectra of phenylacetaldehyde, β-phenylpropionaldehyde (hydrocinnamaldehyde) and γ-phenylbutyraldehyde shown in Fig. 2 show that only the α-phenyl compound has a band with a pronounced maximum in the 290–310 mμ region. The β-phenyl compound does have a shelf in this region which could arise from a small band while the γ-phenyl compound does not have absorption in this region other than that expected from the carbonyl group plus the tail of the 260 mμ phenyl band. The fact that only the α-phenyl compound has a pronounced band raises

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(1) Presented before the Physical and Inorganic Section at the San Francisco Meeting of the American Chemical Society, March 30, 1949.

(1a) Fellow, American Foundation for Pharmaceutical Education for 1949–1950.

(2) Webb, *et al.*, *J. Org. Chem.*, **4**, 389 (1939).

(3) Purvis, *J. Chem. Soc.*, 780 (1927).

(4) Ramart-Lucas and Guerlain, *Bull. soc. chim.*, **49**, 1860 (1931).

(5) Arnold and Kistiakowsky, THIS JOURNAL, **54**, 1713 (1932).

(6) Biquard, *Ann. chim.*, **20**, 97 (1933).

(7) Bruzau, *Ann. de chim.*, Ser. II, **1**, 257 (1934).

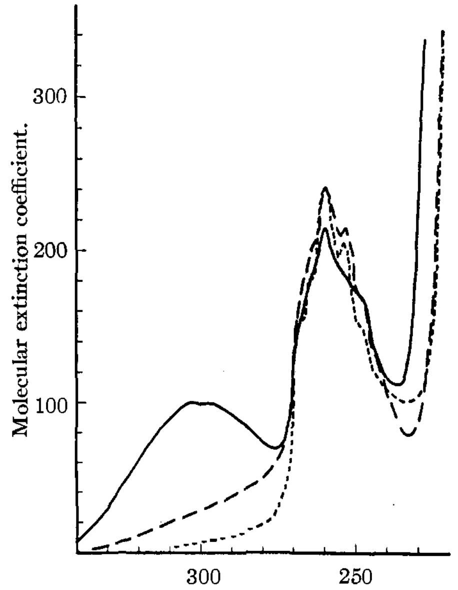

Fig. 2.—Phenylacetaldehyde, —; β-phenylpropionaldehyde, — —; γ-phenylbutyraldehyde, - - -.

the question whether an enol form may not be responsible. This possibility is ruled out by the spectra of the compounds $C_6H_5CH_2-\overset{O}{\overset{/\!/}{C}}-CH_3$, $C_6H_5-\underset{H}{\overset{CH_3}{\overset{|}{C}}}-\overset{O}{\overset{/\!/}{C}}-CH_3$, $C_6H_5-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-\overset{O}{\overset{/\!/}{C}}-CH_3$ shown in Fig. 3. The last compound cannot have any enol, yet the spectra of all three are very similar. These spectra are remarkable in that the long wave length bands have fine structure that is very similar to the fine structure in the bands at 260 mμ associated with the phenyl group.

The spectrum of 3,3-diphenylbutanone-2, Fig. 4, is qualitatively similar but with over twice the extinction coefficient of the monophenyl compound.

Since the spectrum of the carbonyl group shows little if any fine structure, the long wave length band of acetone for example having no fine structure, it seems highly unlikely that the long wave length band is simply an elevated carbonyl band. Rather the large amount of fine structure in this band and the similarity of the fine structure to that in the 260 mμ phenyl band indicates the phenyl group is in major part responsible for this long wave length band also.

The presence of the 295 mμ band in all of the compounds containing a phenyl α to a carbonyl indicates that this band is associated with this type of structure. Furthermore a carbonyl in this position must be able to interact with the ring by a mechanism other than enolization or formation of a ring through a chemical bond. The only path available is through the α carbon atom. This is contrary to the concept that a saturated carbon atom always acts as a good insulator between two resonating systems. It is also contrary to the commonly held working hypothesis that two chromophores when separated by one or more saturated carbon atoms act independently. Evidence is accumulating in the literature that neither of these concepts are strictly true. Woodward[8] has accounted for the longer λ_{max} (255–290 mμ) in a conjugated diene in a six membered ring compared with a λ_{max} (215–250 mμ) in a linear conjugated diene by

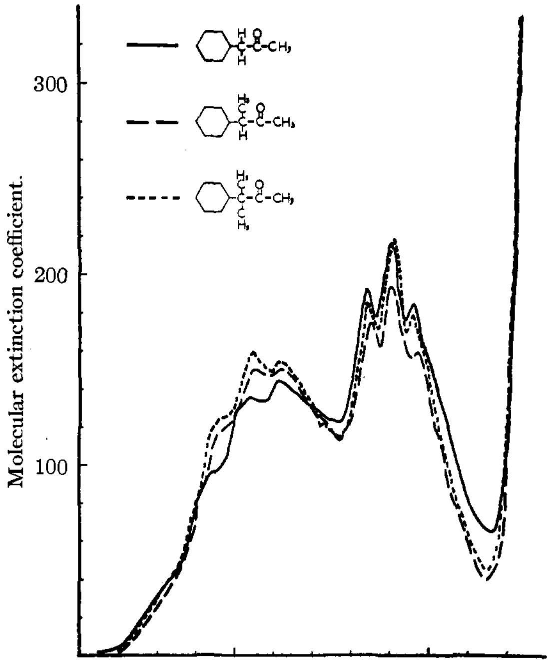

Fig. 3.

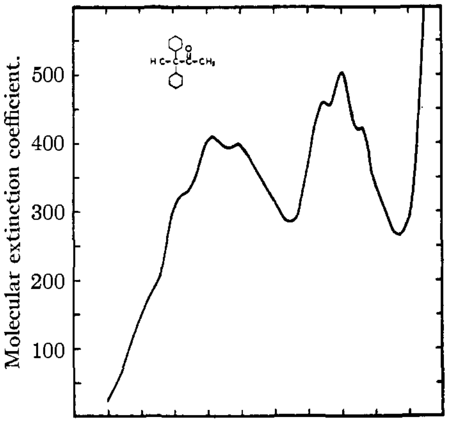

Fig. 4.

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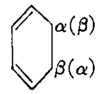
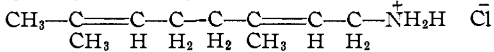
[8] Woodward, THIS JOURNAL, 64, 72 (1942).



assuming that the electrons in the bond α,β to each of the double bonds are sufficiently labilized to permit oscillations almost as long as those in a triene. Jeffrey[9] has found that the central bond in geranylamine hydrochloride is abnormally short,



$CH_3-\underset{CH_3}{C}{=}\underset{H}{C}-\underset{H_2}{C}-\underset{H_2}{C}-\underset{CH_3}{C}{=}\underset{H}{C}-\underset{H_2}{C}-\overset{+}{N}H_2H\ \overset{-}{Cl}$

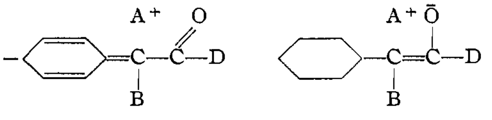
1.44 ± 0.04 Å. as is also the central bond[10] in dibenzyl, 1.48 ± 0.01 Å. These facts were explained by employing the concept of hyperconjugation. This would permit some double bond character to be assumed by the central bond and account for the shortened bond distance.

The ultraviolet absorption spectrum of geranylamine hydrochloride has been investigated by Bateman and Koch[11] who found no departure from a substituted ethylene spectrum. The authors have considered several explanations, the most likely being that the hyperconjugation process affects equally both the normal and the excited states of the molecule. Some of the spectra of dibenzyl reported in the literature have a band at 300 mμ with an extinction of about 35 while other measurements do not show this band. We have measured purified samples of dibenzyl and find no band around 300 mμ. This compound then behaves like geranylamine hydrochloride in that it gives no evidence spectroscopically, of the shortened central bond.

In contrast with these compounds the α-phenyl carbonyl compounds give definite evidence spectroscopically of an interaction between the carbonyl and phenyl groups. The behavior may be associated with the great difference of the chromophores in case of the α-phenyl carbonyl compounds compared with those in the compounds in which the effect is not shown. The two chromophore groups in dibenzyl are identical while in geranylamine hydrochloride they are virtually so.

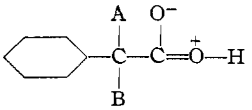
Quantum mechanically the two bands may perhaps be considered as arising from perturbations between the carbonyl and phenyl groups. A theoretical investigation along such lines and also an investigation of bond distances in these compounds is indicated.

At present we prefer to explain the effect in terms of no bond resonance or hyperconjugation. If structures of the type



make contributions the observed spectra would be adequately accounted for. The normal carbon to carbon distances between the α carbon and both the ring and the carbonyl-carbon would be altered by contributions from such structures.

If D were a group of a type that had an unshared pair of electrons and so itself could interact with the carbonyl oxygen we might expect this resonance to be more powerful than that between



the carbonyl group and the ring. If such were the case there would be no, or very little, hyperconjugation or no-bond resonance between the carbonyl and the ring and such compounds would not have a 290–310 mμ band. The spectra of two such compounds, phenylacetic acid and diphenylacetic acid shown in Fig. 5, and likewise the spectra of esters and acid amides which have been measured give no evidence of bands in this region, as is to be expected if our interpretation is correct.

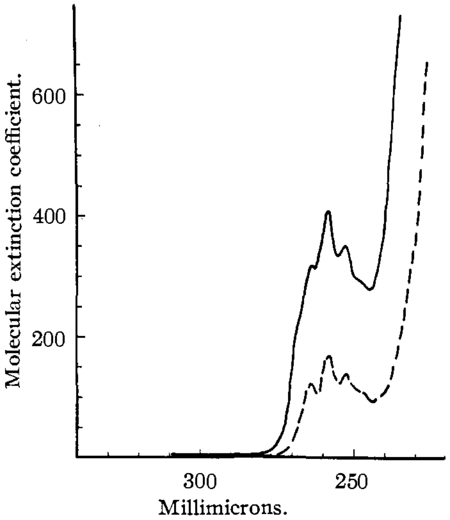


Fig. 5.—Diphenylacetic acid, —; phenylacetic acid, – – –.

Experimental

The absorption spectra were measured in 95% alcohol with a Beckman Quartz Spectrophotometer, Model DU. Solutions were made up in volumetric flasks from weighed quantities of the compounds.

Materials

Methadone (*dl*-Methadon) (*dl*-Amidone Hydrochloride).—Merck and Co. products, recrystallized from ethanol; m. p. 241–242°.

Phenylacetaldehyde.—The Eastman Kodak Co. product was fractionally distilled twice under reduced pressure, b. p. 70–71° at 5 mm.

β-Phenylpropionaldehyde (hydrocinnamaldehyde).—24.5 hydrocinnamic acid (Eastman Kodak Co.) was treated with 23 g. of thionyl chloride in a steam-bath. Excess thionyl chloride was removed under vacuum and the resulting hydrocinnamic acid chloride distilled at 77–78° (2–3 mm.). Rosenmund reduction following the method of "Organic Synthesis," **21**, p. 84, was carried out on the acid chloride. The aldehyde was distilled at 118.5–119°

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[9] Jeffrey, *Proc. Roy. Soc. (London)*, **A183**, 388 (1945).

[10] Jeffrey, *ibid.*, **188**, 222 (1946).

[11] Bateman and Koch, *J. Chem. Soc.*, 600 (1944).

at 11 mm.; yield 10.5 g., 62% of theoretical based on acid chloride.

γ-Phenylbutyraldehyde.—The Grignard was formed in ether with 50 g. of γ-phenylpropyl bromide; 37 g. of freshly distilled ethyl orthoformate was added and the mixture refluxed six hours. The ether was removed by distillation and 200 cc. of chilled 6% hydrochloric acid was added with stirring. The oily layer of acetal was separated and decomposed by distillation with 10% sulfuric acid; 25 g. of sodium bicarbonate in 50 ml. of water was added to the steam distillate and the mixture cooled to 5°. The aldehyde was filtered off and washed; yield 8 g. of impure aldehyde; m. p. 46–48° cor.; 2,4-dinitrophenylhydrazone, m. p. sinters 104°, melts 106–107° cor.

Phenylacetic Acid.—Eastman Kodak Co. (practical) crystallized from isopropyl alcohol; m. p. 76–77°.

Diphenylacetic Acid.—Prepared by the method of "Organic Syntheses," Coll. Vol. I, p. 224, using 120 g. of benzilic acid. The wet product was recrystallized from 600 cc. of 60% ethanol, yield 88.5 g., 72%; m. p. 143–144°. The product gave no red color with concd. sulfuric acid, indicating freedom from benzilic acid.

Dibenzyl.—Eastman Kodak Co. (practical) recrystallized from ethanol, m. p. 52° cor.

Phenylacetone.—Eastman Kodak Co. (practical) phenylacetone was converted to the semicarbazone and recrystallized three times from ethanol, m. p. 186–187°. The semicarbazone was hydrolyzed with 10% phosphoric acid and redistilled, b. p. 69–71° (3 mm.).

3-Phenylbutanone-2 (Phenyl Methyl Acetone).—Prepared by the method of Bruzau[7]: 39 g. of phenylmethylacetonitrile was allowed to react with 100 g. of methylmagnesium iodide in 250 ml. of ether. The ether was distilled off and 200 ml. of dry toluene added. The mixture was refluxed for two hours. Recovery of the ketone was as in the reference cited; yield 12.3 g., 28%; b. p. 78.0–78.5 at (1.5 mm.), $n^{25}\mathrm{D}$ 1.5088. The semicarbazone was prepared and recrystallized four times; m. p. 156–158° cor. The semicarbazone was decomposed with 5% phosphoric acid, redistilled 106–108° (22 mm.), $n^{25}\mathrm{D}$ 1.5085.

3-Methyl-3-phenyl-butanone-2 (Phenyldimethylacetone).—Prepared by the method of Bruzau,[7] 40 g. of phenyldimethylacetonitrile was allowed to react with 181 g. of methylmagnesium iodide (4-fold molal excess) following the same procedure as for 3-phenylbutanone-2; yield 27 g., 61% of theoretical; ketone distilled 76–77° (15 mm.), $n^{25}\mathrm{D}$ 1.5078. The semicarbazone (m. p. 184.5–186.5° cor.) was decomposed with 5% phosphoric acid and redistilled, b. p. 72–74° (2 mm.), $n^{25}\mathrm{D}$ 1.5074.

2,3-Diphenylbutanone-2.—Prepared by method of Sisido and Nozaki, This Journal, **70**, 776 (1948): The semicarbazone was prepared and recrystallized 3 times, final m. p. 177–178° cor., after which it was decomposed by refluxing with 10% phosphoric acid; purified ketone, b. p. 132° (1 mm.), m. p. 39–40°.

Summary

The absorption spectra of some α-phenyl carbonyl compounds have been measured, including phenylacetaldehyde, phenylacetone, phenylmethylacetone (3-phenylbutanone-2), phenyldimethylacetone (3-phenyl-3-methylbutanone-2) *d,l*-methadon hydrochloride, and 3,3-diphenylbutanone-2. β-Phenylpropionaldehyde and γ-phenylbutraldehyde, phenylacetic acid and diphenylacetic acid have also been measured.

All of the α-phenylcarbonyl compounds have a band of unexpectedly high extinction in the 290–310 mμ region. Evidence is presented that neither ring formation nor enolization is responsible but that an interaction between the carbonyl and the phenyl group takes place through the saturated α-carbon atom. An explanation in terms of no-bond resonance has been given for the phenomenon. This behavior indicates that two chromphore groups do not always act independently when separated by a saturated carbon atom and that some resonance interaction takes place through such an atom.

San Francisco, California Received January 17, 1949

[Contribution from the Biology Division, Oak Ridge National Laboratory][1]

Paper Chromatography of Purine and Pyrimidine Derivatives of Yeast Ribonucleic Acid[2]

By C. E. Carter

The application of paper chromatography to problems of nucleic acid chemistry was first reported by Vischer and Chargaff[3] who extended this technique to the quantitative analysis of purine and pyrimidine bases of nucleic acids.[4] The procedure employed consisted of locating the purines and pyrimidines on chromatograms developed with several organic solvents by forming their mercury salts on guide strips and converting this salt to the sulfide. The resultant black spot thus served as a guide for the elution of purines and pyrimidines from untreated areas of the chromatogram. The chromatographic procedure described by Hotchkiss[5] entails the elution of successive areas of the chromatogram developed with butanol and determination of ultraviolet absorption spectra in solutions from these areas for location and quantitation of purines, pyrimidines, and several nucleosides.

This paper describes chromatographic techniques for resolving mixtures of the purines, pyrimidines, nucleosides and nucleotides of yeast nucleic acid and a method for locating these compounds on chromatograms by ultraviolet fluorescence.

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(1) Operated by Carbide and Carbon Chemicals Corporation under Contract No. W-7405-eng-26 for the Atomic Energy Commission, Oak Ridge, Tennessee.

(2) Since submitting this manuscript for publication two notes have appeared dealing with the detection of purines and pyrimidines by fluorescence on paper chromatograms (R. Markham and J. D. Smith, *Nature*, **163**, 250 (1949); and E. R. Holiday and E. A. Johnson, *ibid.*, **163**, 216 (1949)), and a note on paper chromatography of nucleotides employing an isobutyric acid solvent system (E. Chargaff, B. Magasanik, R. Doniger and E. Vischer, This Journal, **71**, 1513 (1949)).

(3) E. Vischer and E. Chargaff, *J. Biol. Chem.*, **168**, 781 (1947).

(4) E. Vischer and E. Chargaff, *ibid.*, **176**, 703 (1948).

(5) R. D. Hotchkiss, *ibid.*, **175**, 315 (1948).