

ketone $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}_2$. This structure could account for the band in propargylic alcohols, but offers no solution in the case of the bromides. This makes the explanation of the band in bromides essentially different from that in the alcohols, since it would be attributed to the allenic group in the bromides and to the ketone group in the "alcohols." This is unlikely in view of their similar behavior, and casts doubt on the postulate. (It is assumed that the enol form is far less prevalent than the keto form.)

4. **The Band May Be a Characteristic Fundamental Frequency of These Molecules or, More Precisely, of the Conventional Molecular Structures Written in Table I.**—This seems highly unlikely. The nearest fundamental on the high wave number side, the $\text{C}\equiv\text{C}$ band, is in its normal position. Similarly the nearest fundamental on the other side, the methylene deformation frequencies near 1450 cm.^{-1} (6.9μ), are in their normal position (see, for example $\text{H}-\text{C}\equiv\text{C}-\text{CH}_2\text{Br}$, compound II). Consequently we reject this explanation.

None of these four explanations is convincing,

and we must conclude that we do not know why these compounds exhibit this band. It may be worth noting that there are other properties of these compounds which are also unusual and which have not been clearly understood. For example the carbon-halogen bond length has been shown to be surprisingly long in propargyl chloride, bromide and iodide by electron diffraction measurements.⁸ The ease with which propargylic alcohols can be rearranged into unsaturated aldehydes and ketones⁹ and the fact that propargylic bromides yield acetylenic and allenic products⁹ should also be kept in mind when the structure of propargylic compounds is considered.

Summary

Infrared spectra of eighteen propargylic halides and alcohols have been measured. Many of these spectra exhibit a band in the range of 1740 to 1600 cm.^{-1} which may be very intense. The reason for a band at this position is still not known.

(8) Pauling, Gordy and Saylor, *THIS JOURNAL*, **64**, 1753 (1942).

(9) For a recent review of the Meyer-Schuster rearrangement, see Hennon, Davis and Maloney, *ibid.*, **71**, 2813 (1949); MacGregor, *ibid.*, **70**, 3953 (1948); Chanley, *ibid.*, **70**, 244 (1948).

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA AND THE BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND]

A Spectroscopic Study of *cis*- and *trans*-Dibenzoylethylenes and Related Compounds

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It is the purpose of this paper to show how the spectra of various dibenzoylethylenes and related compounds are affected by geometrical isomerism and by the introduction of substituents, and to determine what spectral characteristics there are which can enable one to distinguish a more stable isomer from its less stable counterpart in various pairs of geometric isomers. The absorption spectra were obtained in the ultraviolet and the infrared.

The important resonance forms of the dibenzoylethylenes are shown as formulas A, B, C and D. For all of these resonance forms to contribute to the actual state of the molecule it is necessary that the molecule be planar. The relative stability of each member of a pair of isomers will depend largely upon the resonance energy of each isomer, the larger the resonance energy the more stable the molecule. The resonance energy of a molecule will be large when the energy of the various important resonance forms lie close together. Form A is of lower energy than the other forms and both electrostatic and steric factors can raise the energy of the other forms thus decreasing the resonance energy of the molecule.

In dibenzoylene ($\text{R} = \text{R}' = \text{H}$) the *trans* isomer would be expected to be more stable than the *cis*. Each oxygen atom is at the negative end of a dipole and tends to repel the other thus raising the energy of the B, C and D forms of the *cis* isomer where they are required to lie close together. Furthermore as shown in Fig. 1,⁴ the oxygen atoms of the *cis* isomer overlap thus interfering with the planarity of the molecule. Actually the *trans* isomer has been found to be more stable than the *cis*, since the *cis* is converted to *trans* catalytically by acid, base or iodine.⁵

In the case of methyl dibenzoylene ($\text{R} = \text{H}$, $\text{R}' = \text{methyl}$) the choice of the more stable isomer is not so obvious. The electrostatic factor favors the *trans* isomer because in the *cis* isomer, as in the case of the parent compound cited above, the oxygen atoms must lie close to each other. Inspection of Fig. 1 shows that the amount of overlap in each isomer is about the same; the methyl group overlaps the oxygen of the *trans* isomer to about the same extent as the oxygens of the *cis* isomer overlap each other, and the overlap of the methyl groups with the hydrogen

(4) For data on which drawing is based, cf. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

(5) Lutz, *THIS JOURNAL*, **62**, 3423 (1930); (b) Conant and Lutz, *ibid.*, **45**, 1303 (1923); (c) Paal and Schülze, *Ber.*, **35**, 168 (1902).

(1) Aberdeen Proving Ground.

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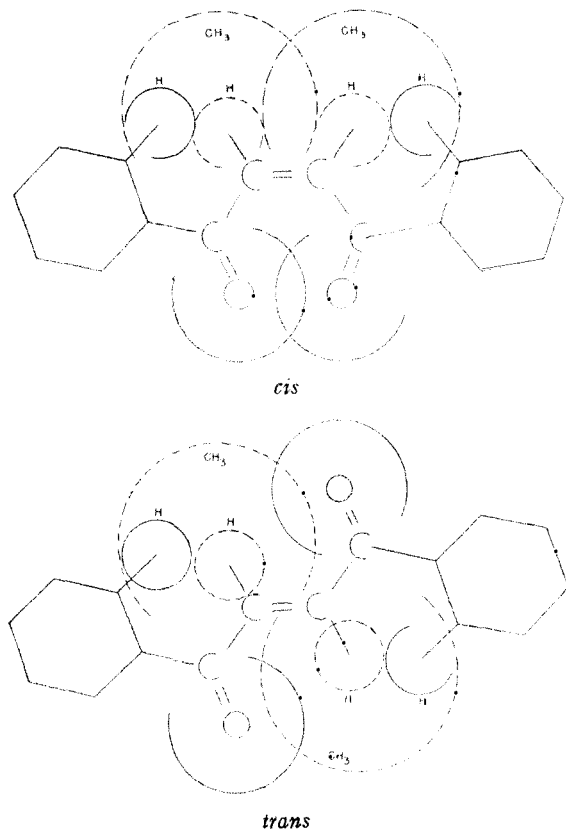


Fig. 1.—Scale drawing of *cis*- and *trans*-dibenzoyl ethylenes based on the following dimensions: bond lengths, C—C, 1.54; C=C, 1.33; C—H, 1.08; C=O, 1.22; atomic radii, H, 0.75; O, 1.4; CH₃, 2.0; bond angles C=C—O, 116°; C=C—C, 116°.

(see Fig. 2) and that the *cis* isomer of a mono-substituted dibenzoyl ethylene is more stable than the *trans* when the substituents are either methyl, bromine or phenyl, which were the only substituents studied.

It has been shown by previous workers^{10,11} that the introduction of a methyl group into a compound containing a conjugated unsaturated carbonyl grouping results in a displacement of λ_{\max} toward the longer wave lengths. However, if the methyl group interferes with the planarity of the molecule, an opposite effect may be superimposed. From Table I it can be seen that in the *trans* series the introduction of one methyl group reduces the wave length of the absorption maximum and the introduction of two methyl groups reduces it still further. In the *cis* series the first methyl group increases or has no effect upon the maximum and two methyl groups decrease the maximum. In dibenzoylacetylene there is no steric hindrance and here the absorption curve is very similar to that of *trans*-dibenzoyl ethylene. In methyl dibenzoyl ethane forms C and D make no contribution since the carbon atoms are saturated and the curve obtained is not very different

(11) Woodward, *This Journal*, **63**, 1128 (1941); **64**, 76 (1942).

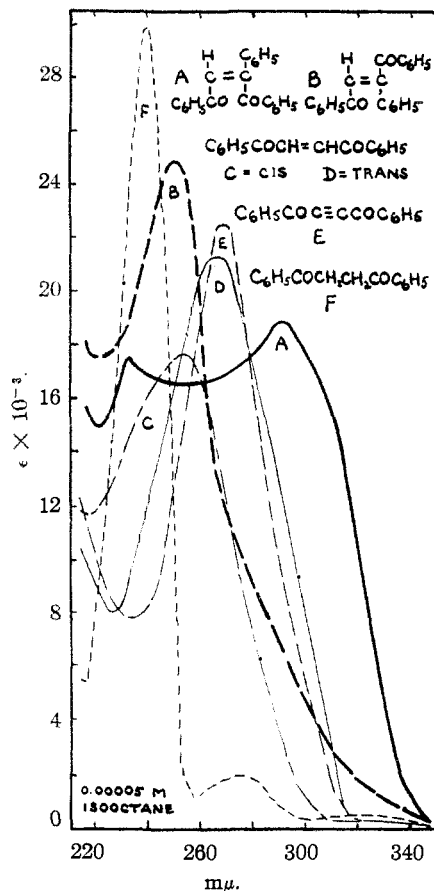


Fig. 2.

from that of *trans*-dimethyldibenzoyl ethylene in which the C and D forms are prevented from making much of a contribution because of steric hindrance.

The spectrum of *cis*-phenyldibenzoyl ethylene which is the stable isomer,¹² is quite different from the spectrum of the other dibenzoyl ethylenes (Fig. 2). This compound can be considered to be a benzoyl-substituted *trans* benzalacetophenone rather than a substituted *cis*-dibenzoyl ethylene and the two bands arise from two essentially isolated chromophores: the band at 291 $m\mu$ is due to the *trans*-benzalacetophenone portion of the molecule and is quite similar to the band of *trans*-benzalacetophenone itself which is found at 298 $m\mu$.¹³ The band at 234 $m\mu$ is due to the isolated benzoyl group which in a compound like dibenzoyl ethane has a band at 240 $m\mu$. The structure of this compound is shown in IV. The benzalacetophenone portion of the molecule is in one plane which is perpendicular to the plane of the benzoyl group. The *trans* isomer (V) has a spectrum like that of the other dibenzoyl ethylenes indicating that in this case the di-

(12) (a) Olivieri-Mandala, *Gazz. chim. Ital.*, **45**, II, 138 (1915); (b) Lutz and Bauer, result to be published shortly.

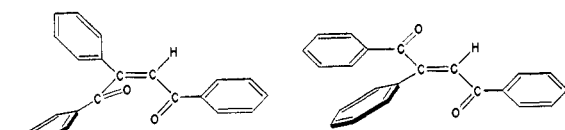
(13) (a) Fischer, *Ber.*, **7**, 1191 (1874); (b) Cromwell and Watson, *J. Org. Chem.*, **14**, 411 (1949).

TABLE I
 SPECTRAL ABSORPTION DATA FOR DIBENZOYLETHYLENE AND RELATED COMPOUNDS

Compound	Isomer	In ethanol		In isoöctane		C=O frequency in infrared: λ in microns
		λ_{\max} in $m\mu$	$\epsilon \times 10^{-3}$	λ_{\max} in $m\mu$	$\epsilon \times 10^{-3}$	
Dibenzoyl ethylene	<i>cis</i>	260	18.1	253	17.8	6.06
Dibenzoyl ethylene	<i>trans</i> ^a	269	18.2	265	21.4	6.14
Dibenzoyl acetylene	...	272	21.4	267	22.7	6.14
Dibenzoyl ethane	...	244	26.5 ^c	240	30.1 ^d	6.00
Methyl dibenzoyl ethylene	<i>cis</i> ^e	258	22.1	254	24.3	6.06
Methyl dibenzoyl ethylene	<i>trans</i>	260	21.7	258	23.4	6.05
Methyl dibenzoyl ethane				241	27.0 ^e	
Dimethyl dibenzoyl ethylene	<i>cis</i>	252	13.0	249	15.7	6.05
Dimethyl dibenzoyl ethylene	<i>trans</i>	250	25.4	245	29.7	6.04
Bromodibenzoyl ethylene	<i>cis</i>	268	23.4	265	22.1	6.07
Bromodibenzoyl ethylene	<i>trans</i>	261	18.5	258	18.4	6.02-6.10
Dibromodibenzoyl ethylene	<i>cis</i>			260	20.0 ^f	6.03
Dibromodibenzoyl ethylene	<i>trans</i>			257.5	25.9 ^g	6.03
Bromodibenzoyl ethane				247	23.5 ^h	
Phenyl dibenzoyl ethylene	<i>cis</i> ^a	302	21.0	291	18.9	6.06
Phenyl dibenzoyl ethylene		235	16.9	233	17.6	6.40 ^b
Phenyl dibenzoyl ethylene	<i>trans</i>	258	29.6	250	25.0	6.08
Phenyl bromodibenzoyl ethylene	<i>cis</i>			256	27.3	
Phenyl bromodibenzoyl ethylene	<i>trans</i> ^a			255	31.1	
Diphenyl dibenzoyl ethylene	<i>cis</i>	255	27.3	255	28.9	
Diphenyl dibenzoyl ethylene	<i>trans</i> ^a	254	32.4	252	32.9	
Phenyl dibenzoyl ethane	...			241	28.8 ^d	
Dimesityl ethylene	<i>cis</i>			276	6.0	6.05
Dimesityl ethylene				239	11.8	
Dimesityl ethylene	<i>trans</i> ^a			275	2.4	
Dimesityl ethylene				235	20.8	6.03
Dimesityl acetylene	...			295	8.0	6.06
Dimesityl acetylene				234	13.2	
Dimesityl ethane	...			240	5.6	
Benzalacetophenone	<i>cis</i>			247	14.0	6.04
Benzalacetophenone				289	8.9	
Benzalacetophenone	<i>trans</i> ^a			225	12.2	6.06
Benzalacetophenone				298	23.7	

^a These are known by independent evidence to be the more stable isomers. ^b It is not certain that this band is due to the carbonyl group. Secondary absorption maxima in $m\mu$ and $\epsilon \times 10^{-3}$; ^c 300, 0.6; ^d 278, 2.0; ^e 278 (bifurcated), 1.7; ^f 292^k, 7.0; ^g 300^k, 2.4; ^h 290^k, 1.9; ⁱ 272, 2.2 (in these cases this secondary absorption is the approximate center point between two inflections on the main curve).

benzoyl ethylene portion of the molecule is more or less planar and the phenyl group is in a plane perpendicular to it.

IV *cis*, stable.V *trans*, labile.

The introduction in two cases of a second substituent into the *cis*-phenyl-dibenzoyl ethylene to give on the one hand *cis*-diphenyl- and on the other *cis*-phenyl-bromo-dibenzoyl ethylene^{12b} results in the disappearance of the benzalacetophenone band and in the appearance of a band similar to that of the other disubstituted dibenzoyl ethylenes at about 250 $m\mu$.

The steric inhibition of resonance is greatest in the dimesityl ethylenes where the *trans* isomer

has its band at 234 $m\mu$ and the *cis* at 239 $m\mu$, and where in both isomers there is in each case only weak absorption at greater wave lengths. Dimesityl acetylene¹⁴ shows similar absorption characteristics, whereas dimesityl ethane absorbs weakly at 240 $m\mu$ and not at all at greater wave lengths.

The isomeric benzalacetophenones have also been included in this study.¹⁵ The *cis* isomer, as will be seen from formula VI, would be expected to be the less stable since the phenyl must overlap the carbonyl and cannot be coplanar with it. This is borne out by experiment. The long wave length band is at 298 $m\mu$ for the *trans* isomer, with an extinction of 23.9.¹³ The corresponding band for the *cis* isomer, which is the labile one, is at a shorter wave length, 290 $m\mu$, and is much

(14) For description of this compound see Lutz and Smithey, results to be published shortly.

(15) For the preparation of the new *cis* isomer, see Lutz and Jordan, THIS JOURNAL, 72, 4090 (1950).

TABLE II
 INFRARED ABSORPTION BANDS OF DIBENZOYLETHYLENES IN MICRONS

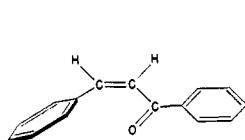
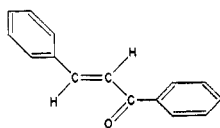
s means strong, m medium, and w weak intensity. Bands in the region of 3.4 and 6.8-7.3 microns were not included since these were obliterated by the mineral oil which has strong bands in these regions.

Dibenzoyl- ethylene		Methyl- dibenzoyl- ethylene		Dimethyl- dibenzoyl- ethylene		Dibenzoyl- acetylene
<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	
6.06 s	6.14 s	6.06 s	6.05 s	6.05 s	6.04 s	6.14 s
6.30 s	6.29 m	6.20 m	6.18 w	6.12 m	6.27 m	6.33 m
6.37 w	6.36 w	6.36 w	6.31 w	6.26 m	6.33 w	6.86 m
7.75 w	7.59 s	7.70 w	7.70 w	6.34 w	7.62 m	8.00 s
8.20 s	7.80 s	7.97 m	7.95 s	7.60 m	8.00 s	8.40 m
8.44 m	8.42 s	8.21 s	8.20 w	7.80 s	8.50 m	8.60 m
8.55 w	8.53 m	8.52 w	10.00 m	7.95 m	9.20 w	9.30 w
9.35 w	8.63 m	9.55 w	10.70 w	8.30 m	9.30 w	9.50 m
9.72 m	9.68 m	10.05 m	13.0 w	8.55 m	10.00 m	9.80 m
9.90 m	9.82 s	10.16 m	13.60 m	9.10 w	10.35 m	10.20 w
10.00 m	9.98 w	10.40 w	14.15 m	9.30 w	12.40 w	12.58 m
10.30 w	10.10 w	11.50 w	14.50 m	9.95 m	13.35 m	12.90 w
10.68 m	10.30 m	11.80 m		10.40 s	13.95 s	14.20 s
11.20 m	12.50 w	12.60 w		11.20 w		
12.18 m	13.10 w	12.88 m		11.70 w		
12.80 m	14.30 s	13.85		12.45 m		
13.12 m		14.20 s		13.30 w		
13.65 m		14.50 w		13.8-		
				14.00 s		
14.10 s				14.40 m		
14.5 m						
Methyl- dibenzoyl- ethane	Phenyl- dibenzoyl- ethylene		Bromo- dibenzoyl- ethylene		Diphenyl- dibenzoyl- ethylene	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
6.00 s	6.06 s	6.08 s	6.07 s	6.02	6.03 s	6.03 s
6.30 m	6.25 m	6.20 w	6.30 w	6.10 s	6.27 m	6.27 m
6.27 w	6.40 s	6.27 m	6.36 w	6.20 w	7.65 m	6.34 w
7.47 m	7.62 m	6.34 w	7.50 s	6.30 s	7.98 m	7.62 m
7.90 w	7.80 m	7.60 m	8.25 s	6.35 w	8.10 s	8.10 s
8.11 m	8.15 s	8.00 s	8.53 w	7.60 m	8.53 m	8.53 m
8.28 s	8.28 w	8.15 s	9.72 w	8.00 s	9.21 m	9.52 m
8.50 w	8.48 m	8.50 m	9.88 m	8.20 w	9.30 m	9.61 m
10.02 m	9.60 m	9.40 m	10.02 w	8.53 m	9.72 w	10.70 w
11.28 s	9.75 m	9.65 m	10.70 w	9.30 m	9.83 w	12.25 w
11.90 w	9.85 m	9.83 m	11.00 w	9.40 m	10.70 w	12.85 m
12.68	10.00 m	10.00 m	12.90 m	9.78 m	11.00 w	13.75 s
13.08 m	10.77 m	10.85 w	13.10 m	9.88 m	12.50 m	14.78 s
13.75 m	10.85 m	11.20 w	13.90 m	10.00 m	13.60	
14.10 s	11.50 w	11.50 m	13.10 m	10.62 w	14.10 m	
14.50 m	12.30 w	12.60 m	13.90 m	11.30 w	14.60 m	
	12.70 w	12.75 w	14.20 m	11.80 w		
	13.05 s	13.10 m	14.60 m	12.53 m		
	13.70 m	13.65 m		13.00 m		
	14.25 m	13.85 s		14.10-		
	14.65 m	14.40 m		14.30 s		
Dimesityl- ethylene		Dimesityl- acetylene		Benzalacetophenone		
<i>cis</i>	<i>trans</i>			<i>cis</i>	<i>trans</i>	
6.05 s	6.03 s	6.06 s	6.04 s	6.04 s	6.06 s	
6.25 s	6.20 m	6.21 m	6.27 s	6.27 s	6.24 s	
8.10 s	7.70 w	7.97 s	6.38 m	6.38 m	6.35 w	
8.67 m	7.93 s	8.06 m	7.70 w	7.70 w	7.50 s	
9.70 m	8.24 m	9.60 m	8.18 s	8.18 s	7.65 m	
9.90 m	8.60 m	9.43 s	9.30 w	9.30 w	7.80 m	
10.00 m	9.52 s	10.14 w	9.70 w	9.70 w	8.25 s	
11.35 m	9.80 w	11.70 m	9.91 s	9.91 s	9.65 w	
11.70 s	10.10 m	13.40 m	10.02 m	10.02 m	9.85 m	

TABLE II (Continued)

Dimesitylolethylene		Dimesityl- acetylene	Benzalacetophenone	
<i>cis</i>	<i>trans</i>		<i>cis</i>	<i>trans</i>
12.35 w	11.20 m	14.00 m	10.83 m	10.10 m
	11.74 s		11.30 m	13.35 s
	12.95 w		12.19 m	14.60 m
	13.35 w		12.76 s	
	13.90 m		13.02 m	
			13.60 s	
			14.20 s	
			14.50 s	

weaker, but there is another and fairly strong band at $248 \text{ m}\mu$, $\epsilon \times 10^{-3} = 1.34$, which corresponds very closely to the band for methyl vinyl ketone which is at $247.5 \text{ m}\mu$.^{13b}

VI *cis*, labile.VII *trans*, stable.

Infrared Spectra.—The observed absorption bands are listed in Table II. Attention was directed to the 6 micron region (see also Table I) which contains the bands due to carbonyl groups and to ethylenic groups. These can usually be distinguished from each other since the latter are generally at slightly longer wave length and are much weaker. It has been shown by Hartwell, Richards and Thompson¹⁶ that the exact position of the carbonyl band is determined by the amount of single bond character possessed by the carbonyl bond. The greater the contribution of structure containing the grouping $\text{C}^+ \text{—} \text{O}^-$, the longer is the wave length at which the band will appear. One would expect therefore that the structural changes which produce a bathochromic effect upon the ultraviolet spectrum would produce a similar effect upon the carbonyl frequency in the infrared. Inspection of Table I which contains the wave length of the carbonyl bands of the compounds studied shows that this is indeed the case in a qualitative way; however the difference between the wave lengths of the carbonyl bands are much smaller than are the differences between the maxima of the absorption bands in the ultraviolet, there being only a difference of 0.1 micron between the longest wave length, that shown by dibenzoylacetylene, and the shortest, that shown by methylidibenzoyl-ethane, and with our instrument the wave lengths can only be read to an accuracy of 0.02 micron. For this reason and because it is not easy to determine extinction coefficients of the infrared bands the ultraviolet spectrum is more suitable for distinguishing a more stable from a less stable isomer.

The compound *cis*-phenyldibenzoylethylene shows a very intense band at 6.4 microns. This wave length is rather long for either a carbonyl or an ethylenic band and it is too strong for the

latter. It may not be fortuitous that this compound which is the only member of the series possessing two intense bands besides the benzene ring band in the 6 micron region, is also the only one having two intense bands in the near ultraviolet. As might be expected the band due to the ethylenic group at about 6.1 microns is stronger for the *cis* compounds than for the *trans* since the stretching of the double bond is accompanied by a greater change in dipole moment in the case of the *cis* isomers. The moderately intense bands at about 6.2 and the weak bands at about 6.25 microns are due to the benzene ring in the benzoyl group.

Further studies in this field are in progress, including an investigation of the β -aroylacrylic acids and related compounds.

Acknowledgment.—Some of the ultraviolet absorptions were determined by Mr. Spencer M. King.

Experimental

Ultraviolet absorptions were determined using a Beckman DU quartz spectrophotometer, and solution concentrations of 0.00005 *M*. The solvents, isoöctane (2,2,4-trimethylpentane) and absolute ethanol, were distilled and their transmissions were checked against distilled water. In Fig. 2 are given typical absorption curves.¹⁷

The **infrared absorption** curves were obtained with a Baird Associates spectrometer equipped with a rocksalt prism. The samples were milled in mineral oil.

Summary

The relative stability of members of various pairs of geometric isomers of dibenzoylethylenes has been discussed.

Ultraviolet absorptions were determined. In every case studied the extinction coefficient is larger for the more stable isomer. The effect of substituents upon the spectra has been shown. The spectrum of *cis*-phenyldibenzoylethylene is that of a substituted benzalacetophenone rather than that of a dibenzoylethylene.

A relationship has been pointed out between the λ_{max} of the ultraviolet band and the position of the carbonyl frequency in the infrared.

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(16) Hartwell, Richards and Thompson, *J. Chem. Soc.*, 1436 (1948).

(17) Other curves from which some of the values in Table I were obtained, are included in a doctorate dissertation submitted to the University by the junior author (C. R. Bauer) August, 1950.