[Contribution from the Avery Laboratory, University of Nebraska and Department of Chemistry, University College, London]

THREE-RING CARBONYL HYPERCONJUGATION IN *CIS* AND *TRANS* ARYL-AROYL ETHYLENE IMINES AND RELATED COMPOUNDS[1]

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In a previous (1) investigation only the *trans* form of 1-methyl-2-phenyl-3-(*p*-toluyl)ethylenimine was isolated and characterized although the presence of the *cis* form in the reaction mixture was indicated. We have now synthesized and separated the *cis* and *trans* racemic forms of 1-cyclohexyl-2-phenyl-3-(*p*-phenylbenzoyl)ethylenimine, IA and IB, and of 1-methyl-2-phenyl-3-(*p*-phenylbenzoyl)ethylenimine, IIA and IIB. These compounds were prepared in excellent yields from 4′-phenylchalcone dibromide and the corresponding primary amines.

The isomers IA and IB were obtained in nearly equal amounts while approximately three parts of IIB to one part of IIA were formed in the reaction with methylamine. Referring to the structural formulas in Chart 1 it is seen that the amount of steric crowding should be nearly equal in the *cis* and *trans* forms, IA and IB, respectively. In IA we find the phenyl and the *p*-phenylbenzoyl group on the same side of the plane of the three-ring, while in IB the cyclohexyl group is on the same side of the plane of the three-ring with the *p*-phenylbenzoyl group, or, as in IB′, on the other side with the phenyl group. We have obtained no physical or chemical evidence for the presence of two such forms of the *trans* isomers although they may exist in some cases in dynamic equilibrium with each other. It seems probable that steric crowding would allow the *cis* form to exist only in the one structure, IA, as indicated, especially since the group on nitrogen is large. In the N-methyl series it is seen that steric crowding in IIA is considerably greater than in either of the possible *trans* forms, IIB or IIB′. Thus when the group on nitrogen is as small as methyl the *trans* forms predominate in the reaction mixtures.[2]

The higher-melting *cis* isomers IA and IIA reacted with phenylhydrazine to give the same pyrazole, 1,5-diphenyl-3-(*p*-xenyl)pyrazole (III). The lower-melting *trans* forms IB and IIB produced the 4-cyclohexylamino- and 4-methylamino-1,5-diphenyl-3-(*p*-xenyl)pyrazolines, IV and V, respectively. This characteristic differential behavior of the *cis* and *trans* ethylene imine ketones with

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[1] A portion of the material in this paper including all of the theoretical discussion was presented at the International Meeting of Spectroscopists, Basle, Switzerland, June 28, 1951.

[2] Since the *trans* forms of the ethylenimine ketones are the more soluble and thus the more difficult to isolate from these mixtures it could be that they are always present in larger amounts. In a coming paper Southwick and Christman, *J. Am. Chem. Soc.*, **74**, May, 1952 have obtained only the *trans*-isomers from a different method of synthesis. Their addition of the N-iodo amines to the *trans*-benzalacetophenone might be expected to give mainly (A), in a concerted *trans*-addition process to the C═C bond. The addition product

phenylhydrazine has been discussed previously (1). The diagnostic ultraviolet spectra for III, IV, and V are given in Fig. 1.

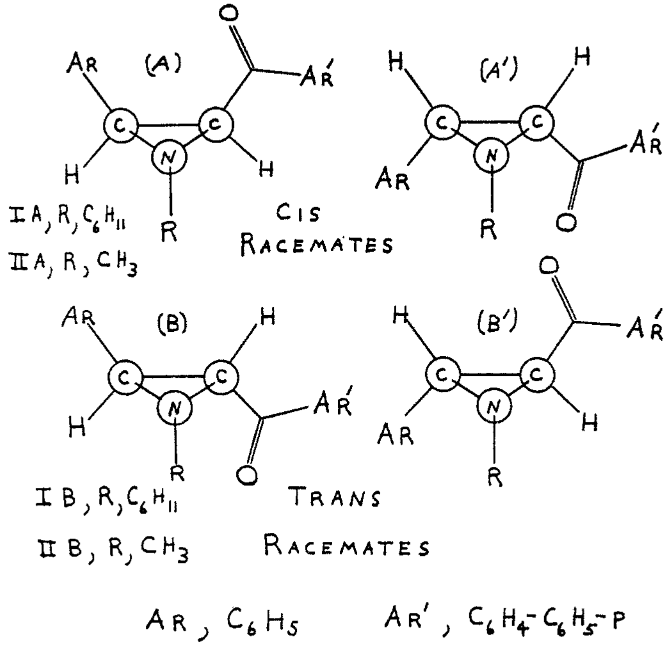

CHART 1

Three-ring conjugation with unsaturated groups. Rogers (2) has discussed the electron interaction of the so-called loosely held three-ring bonding electrons of the cyclopropane and ethylene oxide rings with the π-electrons of such unsatu-

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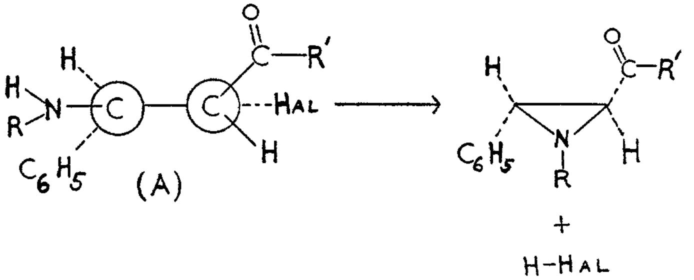
(A) would then be of such a configuration as to close the ring by an internal SN_2 reaction to give mainly the *trans*-ethylenimine ketone.



Since these ring closures are usually, if not always, of an internal SN_2 type this means that in our reactions of amines with the α,β-dibromoketones and the α-bromo-α,β-unsaturated ketones the intermediate α-bromo-β-aminoketones must exist as varying mixtures of the two diastereoisomers, one of which leads to the *trans*-, the other to the *cis*-ethylenimine ketone. One might expect even the 1,4-addition of the amine to the α-bromobenzalacetophenone (*cis* and/or *trans*) to give mainly the diastereoisomer, racemate (A), which could most readily close the ring to form the *trans*-ethylenimine ketone. The importance of steric control on the variation in the composition of the mixed α-halo-β-aminoketones may be decided by the experiments now underway in this laboratory.

rated groups as the benzene ring, the vinyl group, and the carbonyl group. Roberts, *et al.* (3) have given an excellent discussion of the possible steric requirements for this type of hyperconjugative resonance between the cyclopropane ring and an attached cationic carbon. In an earlier paper (1) we considered briefly the steric effects of large groups attached to the three-ring on such electronic interactions for the *cis* and *trans* ethylene imine ketones. Our previous pictorial representation (1) of these electron interactions was incomplete. Now we wish to set forth in more precise detail a molecular orbital as well as a resonance pictorial representation of these interactions and to discuss some structural variations which might be expected to influence the extent of them.

Walsh (4) and Coulson and Moffitt (5) have given somewhat different descriptions of the endocyclic bonds in cyclopropane but both representations imply considerable *delocalization* and *p-character* for the bonding molecular orbitals. Since the treatment of Coulson and Moffitt (5) lends itself to a qualitative quantum mechanical treatment we shall adopt their symbolism of *bent bonds* in our pictorial description and discussion of the bonding orbitals of the ethylenimine and ethylene oxide rings.

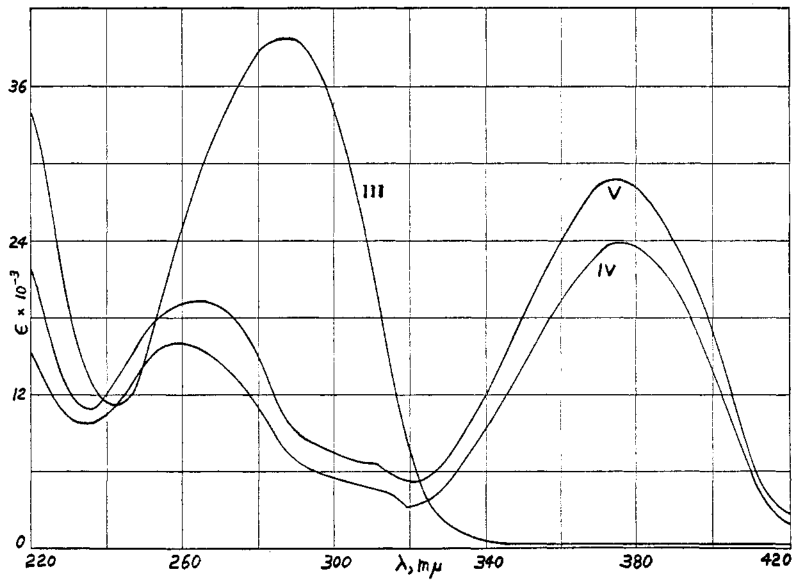


FIGURE 1. ULTRAVIOLET ABSORPTION SPECTRA OF 1,5-diphenyl-3-(*p*-xenyl)pyrazole (III); 4-cyclohexylamino-1,5-diphenyl-3-(*p*-xenyl)pyrazoline (IV); and 4-methylamino-1,5-diphenyl-3-(*p*-xenyl)pyrazoline (V).

The bond distances and bond angles for an ethylenimine have not been reported as yet but the recent accurate measurements of Cunningham and coworkers (6) for ethylene oxide can probably be used without introducing any important error in this qualitative discussion of the ethylenimine ring. As these workers (6) have pointed out, since the carbon to oxygen distances are near normal (1.4363 Å) while the carbon to carbon distance is considerably shortened (1.4728 Å), it would seem that most of the ring strain must be accounted for (accommodated) in this latter bond. We wish to suggest that both ethylene oxide and ethylenimine may be described pictorially as perfect pairing models, indicating that there is more bending of the carbon to carbon bond, *i.e.* more extension of this bonding molecular orbital in the plane of the ring, than for the carbon to oxygen or carbon to nitrogen bonds. It is suggested that the atomic orbitals are directed as indicated by the arrows in Fig. 2 assuming the oxygen and nitrogen atoms to be using their 2px and 2py orbitals (orbital direction angles 92°), while the two carbon atoms are using their hybridized (2s—2pσ) orbitals (5) (orbital direction angles 104°) to form the three-ring endocyclic bent bonds.[3] This type of bonding is intermediate between the side-wise π-bonding overlap and an end-wise sigma bonding overlap.

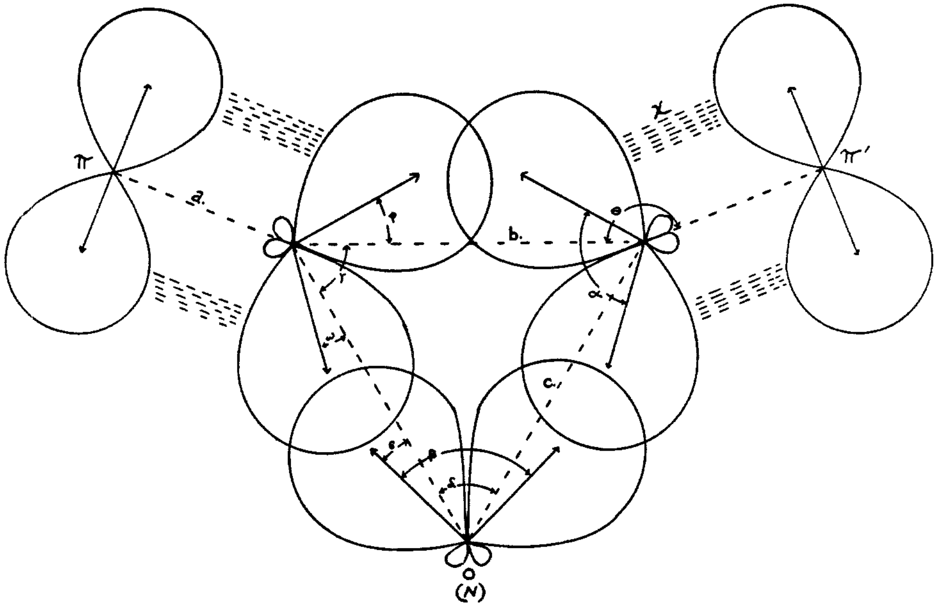


FIGURE 2. A PLANAR PROJECTION DRAWN TO SCALE (EXCEPT FOR ORBITAL VOLUMES) OF an ethylenimine or ethylene oxide *bent bond* orbital model with ρ-electron possessing carbons π and π' attached to the ring carbon atoms. Based on the dimensions: Angles—α, 104°; β, 92°; γ, 59° 9.4′; δ, 61° 41.2′; ϵ, 15° 9.4′; π, 30° 5′; ω, 14° 45.6′; and θ, 158° 5′. Bond distances—a, 0.8 Å (a planar projection of a carbon to carbon distance of 1.53 Å, assuming the measured H—C—H angle of 116° in ethylene oxide); b, 1.47 Å; and c, 1.43 Å.

When atoms with unshared p-electrons (halogen atoms) or with π-bonding electrons (carbon atoms of the benzene ring or carbonyl group) are attached to the carbon atoms of any of these bent bond rings (ethylenimine, ethylene oxide, or cyclopropane) some overlapping and interaction between the bent bonds and the π- or p-orbitals is to be expected as represented by the broken lines x in Fig. 2. This would seem to be the fundamental reason for the low reactivity of

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[3] Subsequent to the preparation of this paper we have seen a more complete report of the careful studies of ethylene oxide (and also ethylene sulfide) by Cunningham and his co-workers, *J. Chem. Phys.*, **19**, 676 (1951) which now includes an interesting description of the probable bonding in this three-ring which is nearly identical with ours.

cyclopropyl chloride in solvolytic reactions which have been classified as manifestations of internal strain by Brown and coworkers (7).

When two unsaturated groups such as an aryl and an aroyl group are attached to the carbons of these three-rings in such a manner as not to sterically interfere with each other (*i.e.*, *trans*-ethylenimines IB and IIB) then both are expected to interact (see Fig. 2), with the bent bonds of three-rings. This dual interaction should produce an additive effect and thus create a more degenerate hyperconjugated system than when only one of the unsaturated groups is present. The planes of the aryl and aroyl groups are nearly perpendicular to the plane of the three-ring. However, the π-orbitals of the unsaturated atoms and the bent bond hybridized orbitals of the two three-ring carbon atoms in these *trans* forms are arranged to meet the maximum overlap requirement (see Fig. 2). This interaction should lead to a discernible increase in the polarization (8) and single-bond character of the carbonyl group in the *trans*-isomers in contrast with the slight interaction in the *cis*-isomers or the simpler compounds having only the aroyl group attached to the three-ring.

When two unsaturated groups are attached to the carbons of these three-rings in such a manner as to sterically interfere with each other than less electron interaction between the unsaturated groups and the three-ring is to be expected (*i.e.* in *cis*-ethylenimine ketones IA and IIA). In such cases it is not likely that orbital overlap will occur between the bent bonds of the three-rings and the π-orbitals of either unsaturated group. The carbonyl groups in such compounds might be expected to have an even lower polarity (less single-bond character) than those of the simpler aroyl three-ring compounds (*i.e.* 1-cyclohexyl-2-(*p*-phenylbenzoyl)ethylenimine).

Modified Lewis structures with partial (δ) charges to pictorially describe the resonance representation of such electron interactions and distributions which can be expected to increase the polarization of the carbonyl group in the *trans* forms of the aryl-aroyl ethylenimines and ethylene oxides are given in Chart 2. This resonance is expected to make a greater contribution to the electronic excited states than to the ground states. Thus the effect of resonance on the ultraviolet spectra may in some cases be more pronounced and discernible than the effect on the infrared spectra. These resonance interactions might be expected to be more pronounced for the ethylenimine ketones than for the epoxy or cyclopropyl ketones. In the ethylenimines the nitrogen atom should be better able to aid in the support of the partial positive charge in the three-ring than would a carbon or oxygen atom. A positive charge in an excited state would seem to be more readily accommodated at the *beta* carbon than at the *alpha* carbon. It is interesting to contrast the opportunities for resonance here with that previously described (9, 10) for the related α-amino- and β-amino-α,β-unsaturated ketones.

The above conclusions have been derived from the previous studies (1, 8) and are confirmed by the experiments reported here. It would be interesting to compare the spectra of isomeric pairs of aryl-aroyl ethylene oxides and cyclopropanes.

Absorption spectra. The ultraviolet absorption spectra for IA and IB are given in Fig. 3; for IIA and IIB, see Fig. 4. The spectral curves for 4′-phenylchalcone and β,*p*-diphenylpropiophenone (VI) are given in Fig. 5. The *p*-phenyl group causes a shift of the maxima toward the red of from 360 to 400 Å for the formally saturated ketones IA, IB, IIA, IIB, and VI, and of 264 Å for the 4′-phenylchalcone, as is seen by comparison with the results obtained for the unsubstituted chalcone series (1, 9).

The characteristic infrared absorption bands to be associated with the carbonyl bond stretching vibrations in the solid compounds were found at the frequencies indicated in the experimental section for IA, IB, IIA, IIB, VI, 4′-phenylchalcone, 1-cyclohexyl-2-(*p*-phenyl)benzoylethylenimine, and *trans*-epoxybenzylacetophenone. The introduction of the phenyl group into the *p*-position of the benzoyl grouping in these compounds causes either no change or a small (about 10 cm^{-1}) shift of the infrared carbonyl band to lower frequencies [see reference (1) for a contrast with the results in the unsubstituted chalcone series]. The location of this carbonyl stretching vibration band is determined by the single bond character of the carbonyl group of the ground state resonance

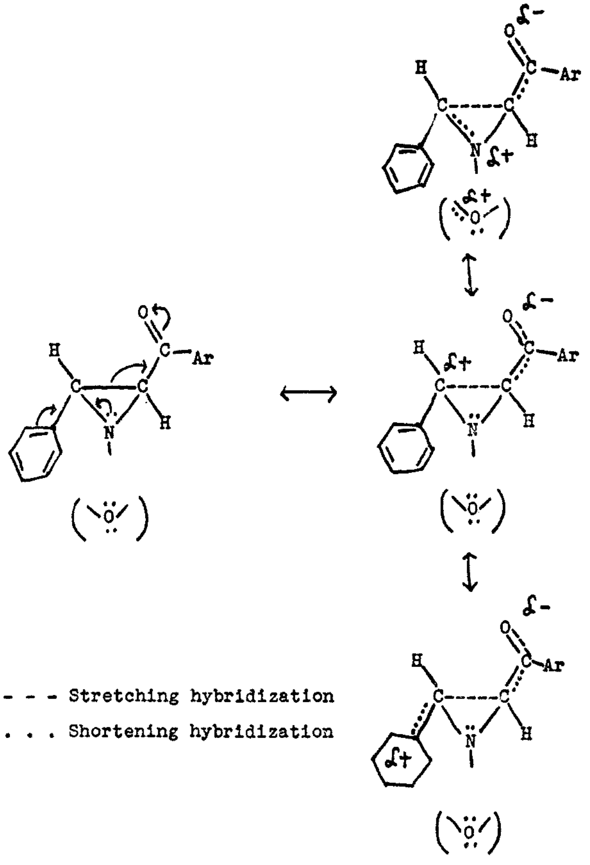


Chart 2. Three-Ring Carbonyl Resonance of Aryl-Aroyl Ethylene Imines and Oxides

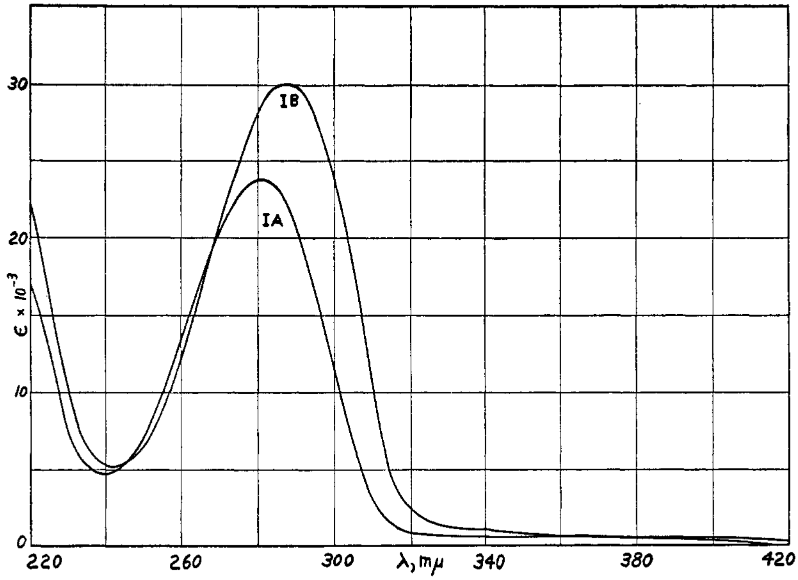


FIGURE 3. ULTRAVIOLET SPECTRA OF 1-cyclohexyl-2-phenyl-3-(*p*-phenylbenzoyl)ethylenimine, *cis* (IA) and *trans* (IB).

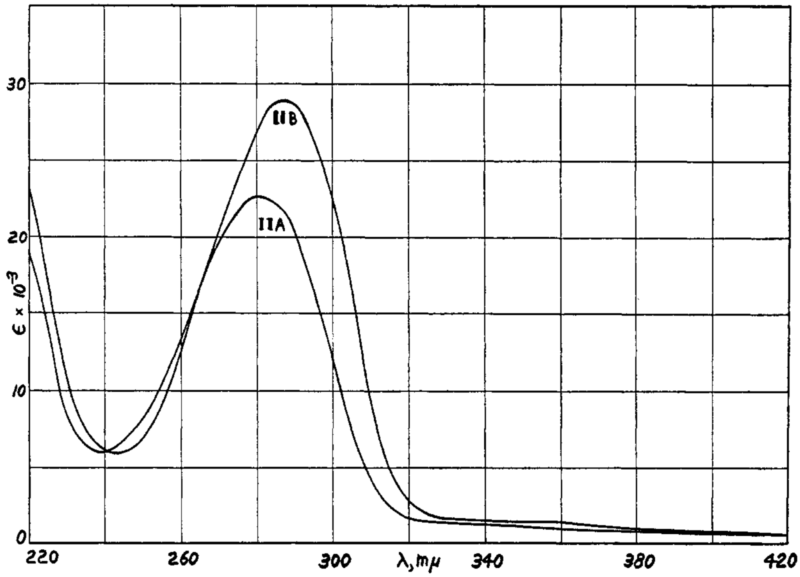


FIGURE 4. ULTRAVIOLET SPECTRA OF 1-methyl-2-phenyl-3-(*p*-phenylbenzoyl)ethylenimine, *cis* (IIA) and *trans* (IIB).

hybrid. The ultraviolet absorption band is associated with the excited state to which resonance in the entire *p*-phenylbenzoyl grouping is apparently able to make a more significant contribution.

Contrary to previous statements (1) it is apparent that the size of the group on nitrogen in the ethylenimine ketones has very little effect on electronic interactions between the three-ring and the carbonyl group. The earlier ultraviolet (1) and present infrared studies with 1-cyclohexyl-2-(*p*-phenylbenzoyl)-ethylenimine clearly indicate that there is very little electron interaction between the three-ring and the carbonyl group here. This confirms the conclusion drawn from the similar studies (1) with 1-cyclohexyl-2-benzoylethylenimine, namely, that it is necessary to have orbital overlap possible with both carbons of the three-ring and attached unsaturated groups to obtain extensive interaction.

Epoxybenzylacetophenone, which in view of its synthesis from *trans*- chalcone and hydrogen peroxide is probably of the *trans*-form, shows three-ring hyperconjugation with the carbonyl group in the excited state as indicated by the ultraviolet studies (abs. max. λ, 250 mμ; ε, 16,800); benzylacetophenone (9) has λ_{max}238 mμ, ε, 12,400; and α-hydroxy-β-morpholinobenzylacetophenone has λ_{max}242 mμ, ε, 11,500 (11). The fact that in *trans*-epoxybenzylacetophenone the characteristic infrared band to be associated with the carbonyl stretching vibration is found at 1687 cm^{-1} [for benzylacetophenone the carbonyl band is at 1685–1690 cm^{-1} (12)] indicates that the expected resonance does not make a significant contribution to the ground state.

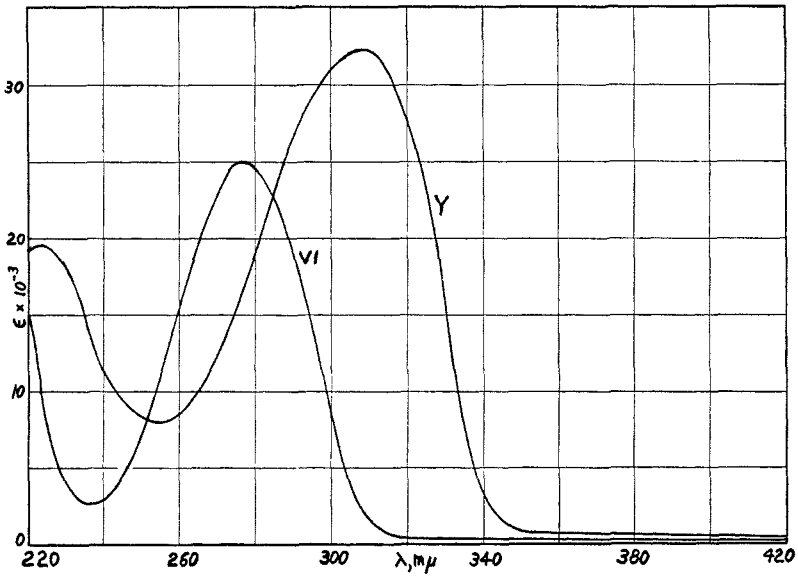


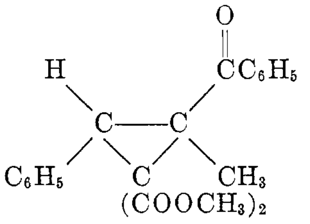
FIGURE 5. ULTRAVIOLET SPECTRA OF β,*p*-diphenylpropiophenone (VI) and 4′-phenylchalcone (Y).

Recently Kuhn and co-workers (13) have shown that *cis*-chalcone has its long wave length band in the ultraviolet at 298 mμ (ε, 8,900), which when contrasted with the value (λ, 298 mμ, ε, 23,700) for the *trans*-form indicates, as they point out, a steric inhibition of resonance. These investigators also reported nearly identical values for the carbonyl stretching frequency in the infrared for the *cis* (1655 cm^{-1}) and *trans* (1650 cm^{-1}) forms of chalcone. Our previous studies (10) and the present ones indicate that further extension of the conjugated system beyond the grouping ($C{=}CCOC_6H_5$) by attaching phenyl groups to the ends is not expected to greatly influence the carbonyl stretching vibration; *i.e. trans*-4′-phenylchalcone also has its carbonyl band at 1657 cm^{-1}.

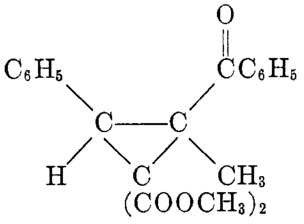
The *cis* arrangement of the aryl and aroyl groups in the α,β-unsaturated ketones is unable to extensively affect the ground state resonance interaction between the benzoyl group and the vinyl group. Such a *cis* arrangement is expected to influence the long wave length absorption in the ultraviolet. The ultraviolet absorption is probably associated with the electronic vibrations and resonance in an ionized excited state of the entire unsaturated system which has difficulty in approaching coplanarity.

There is a fundamental difference in the function of a *beta* aryl group attached to the three-ring carbonyl compounds and in the related α,β-unsaturated ketones. In the former the presence of the aryl group (*i.e.* in a *trans* arrangement) is necessary to create a considerable degree of degeneracy in the three-ring carbonyl hyperconjugated system. In the α,β-unsaturated ketones vinyl unsaturation exists and its interaction with the carbonyl group cannot be inhibited extensively by the *cis* arrangement of the aryl and aroyl groups.

Many years ago Carr and Burt (14) studied two forms (m.p. 101° and 133°) of 1,1-dicarbomethoxy-2-phenyl-3-methyl-3-benzoylcyclopropane. They observed that the lower-melting isomer gave the stronger *general* absorption in the ultraviolet. They suggested that by analogy with the spectra of olefinic compounds which had been studied, the lower-melting isomer might be the *trans*-form. We would agree with this assignment for the reasons given above providing these spectral differences can be verified.



(m.p. 101°, *trans*)



(m.p. 133°, *cis*)

Several investigations are being carried out at present in this laboratory to further check these conclusions concerning three-ring carbonyl hyperconjugation.

Acknowledgment. A portion of the work described here was done by the senior author at University College, London, during 1950–1951 while holding a John Simon Guggenheim Memorial Fellowship and a Fulbright Research Scholarship.

EXPERIMENTAL[4]

4′-Phenylchalcone dibromide. A 272-g. (0.96 mole) sample of 4′-phenylchalcone (15) was dissolved in 1400 ml. of chloroform and treated slowly with 153.6 g. (0.96 mole) of bromine

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[4] Microanalyses for carbon, hydrogen, and nitrogen are by the Clark Microanalytical Laboratory, Urbana, Illinois.

in 100 ml. of chloroform. Concentration of the reaction mixture and recrystallization of the precipitated material from acetone and then from methanol produced 277.0 g. (65% yield) of a colorless solid, m.p. 194–195° (16).

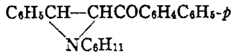
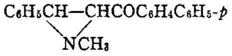
Anal. Calc'd for $C_{21}H_{18}Br_2O$: C, 56.76; H, 3.60.

Found: C, 56.95; H, 3.78.

Cis- and trans-1-cyclohexyl-2-phenyl-3-(p-phenylbenzoyl)ethylenimine, IA and IB. A suspension of 66.6 g. (0.15 mole) of 4′-phenylchalcone dibromide in 350 ml. of dry benzene was stirred at 20–30° for ten hours with 44.6 g. (0.45 mole) of cyclohexylamine. The products were isolated in much the same manner as has been described previously for related isomeric pairs of ethylenimine ketones (17). The lower-melting, more soluble isomer was extracted from the higher-melting form with boiling petroleum ether (b.p. 60–80°). The higher-melting isomer (IA) was obtained as short, colorless needles from methanol and chloroform mixtures, m.p. 144–146°, in a 47% yield. The lower-melting and more soluble isomer (IB) formed pale yellow needles from methanol and chloroform, m.p. 117–118°; yield 44%.

TABLE I

INFRARED ABSORPTION SPECTRA

 $C_6H_5CH{-}CHCOC_6H_4C_6H_5\text{-}p$ with NC_6H_{11} bridging				 $C_6H_5CH{-}CHCOC_6H_4C_6H_5\text{-}p$ with NCH_3 bridging			
IA-*cis*		IB-*trans*		IIA-*cis*		IIB-*trans*	
cm^{-1}	% abs.	cm^{-1}	% abs.	cm^{-1}	% abs.	cm^{-1}	% abs.
3070	vwk broad	3070	vwk	3070	vvwk	3045	vvwk
3050	vwk	3047	vwk	3020	vvwk	3020	vvwk
3020	vwk	3020	vwk	1681	80	1660	70
1685	78	1656	85	1604	53	1606	47
1605	35	1601	60	1585	25	1586	10
1578	20	1583	30	1578	20	1578	10
1498	18	1449	60	1406	25	1418	42
1450	50	1408	73	1376	30	1406	41
1425	25	1363	45	1340	10	1351	33
1374	35	1357	33	1315		1320	
				to	10 broad	to	8 broad
1349	10	1313	30	1308		1315	
1318		1250		1237	52	1297	3
to	10 broad	to	45 broad				
1311		1246		1199	55	1272	2
1260	5	1230	53	1182	40	1250	48
1246	22	1206	46	1160	25	1229	50
1234	45	1197	65	1145	31	1195	50
1199	50	1184	42			1182	37
1184	31	1171	31			1159	30
1160	23	1160	30			1136	30
1154	30	1125	29			1118	23
1122	18						

Anal. Calc'd for $C_{27}H_{27}NO$: C, 85.00; H, 7.13; N, 3.67.

Found for IA: C, 85.25; H, 7.11; N, 3.90.

Found for IB: C, 85.20; H, 7.26; N, 3.90.

The lower-melting isomer IB was also more soluble in moist ether or in 95% ethanol than was IA.

Cis- and trans-1-methyl-2-phenyl-3-(p-phenylbenzoyl)ethylenimine, IIA and IIB. To an ice-cooled suspension of 66.6 g. (0.15 mole) of 4′-phenylchalcone dibromide in 200 ml. of benzene was added a cold ether solution of methylamine (about 0.6 mole of CH_3NH_2). This mixture was allowed to warm to room temperature and was stirred for 28 hours. Isolation of the products gave a 20% yield of IIA as cream-colored needles from methanol, m.p. 138–139°, and a 70% yield of the more soluble IIB as light yellow plates from abs. ethanol, m.p. 120–121°.

Anal. Calc'd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47.
Found for IIA: C, 84.52; H, 5.87; N, 4.51.
Found for IIB: C, 84.10; H, 6.13; N, 4.48.

Reactions of the ethylenimine ketones with phenylhydrazine. In each case 1.9-g. (0.005 to 0.006 mole) samples of the ethylenimine ketone were dissolved in 25 ml. of a 40–60 abs. ethanol-chloroform mixture containing 0.010 to 0.012 mole of glacial acetic acid and 0.006 to 0.007 mole of phenylhydrazine. The mixtures were warmed at 40–50° for 15 minutes to obtain clear solutions, and then allowed to stand 12 hours at room temperature. In the case of IB and IIB, the solutions developed the blue fluorescence, characteristic of the triaryl pyrazolines, almost immediately after mixing. The solutions to which IA and IIA had been added were concentrated somewhat and were cooled in an ice-bath to cause the products to crystallize. Recrystallization from chloroform-abs. ethanol mixtures produced the pyrazol III as identical colorless needles in both cases, m.p. 169–170°; yield from IA, 84% and from IIA, 78%.

Anal. Calc'd for $C_{27}H_{20}N_2$: C, 87.06; H, 5.41; N, 7.52.
Found: C, 87.35; H, 5.41; N, 7.56.

The reaction mixtures of IB and IIB were diluted with more abs. ethanol and cooled in an ice-bath to crystallize the products. The imine IB produced an 86% yield of 1,5-diphenyl-3-(*p*-xenyl)-4-cyclohexylaminopyrazoline (IV) as bright yellow needles from chloroform and ethanol, m.p. 190–191°.

Anal. Calc'd for $C_{33}H_{33}N_3$: C, 84.04; H, 7.05; N, 8.91.
Found: C, 83.71; H, 6.84; N, 8.79.

The imine IIB gave a 56% yield of 1,5-diphenyl-3-(*p*-xenyl)-4-methylaminopyrazoline (V) as yellow needles from chloroform and abs. ethanol, m.p. 172–173.5°.

Anal. Calc'd for $C_{28}H_{25}N_3$: C, 83.34; H, 6.25; N, 10.41.
Found: C, 83.54; H, 6.46; N, 10.52.

Both of the amino pyrazolines, IV and V, gave a positive Raiford pyrazoline test with $FeCl_3$ in conc'd H_2SO_4 solution (blue-green coloration) (18).

β,p-Diphenylpropiophenone (VI). A 1.92-g. (0.0067 mole) sample of 4′-phenylchalcone was dissolved in 200 ml. of ethyl acetate and shaken with hydrogen at 48 p.s.i. in the presence of 0.1 g. of PtO_2 catalyst for ten minutes. The isolated product was recrystallized from methanol and chloroform to give silvery-white plates, m.p. 119–120°; yield 90%.

Anal. Calc'd for $C_{21}H_{18}O$: C, 88.08; H, 6.33.
Found: C, 88.27; H, 6.43.

Absorption spectra measurements. The *ultraviolet* absorption spectra of 2,2,4-trimethylpentane (Spectro Grade, Eastman Kodak Co.) solutions of the compounds were obtained using silica cells and a Beckman Model DU photoelectric quartz spectrophotometer. The maxima for the compounds were found at: for IA, λ, 280 mμ (ε, 23,920); IB, λ, 286 mμ (ε, 30,260); IIA, λ, 281 mμ (ε, 22,850); IIB, λ, 288 mμ (ε, 28,930); III, λ, 289 mμ (ε, 40,020); IV, λ, 375 mμ (ε, 24,070) and λ, 257 mμ (ε, 16,060); V, λ, 375 mμ (ε, 28,980) and λ, 265 mμ (ε, 20,570); VI, λ, 276 mμ (ε, 25,160); 4′-phenylchalcone, λ, 223 mμ (ε, 19,500) and λ, 310 mμ (ε, 32,630). See Figs. 1, 3, 4, and 5 for the complete spectral curves.

All *infrared* studies were done with Nujol mulls of the compounds using a Perkin-Elmer Model 12 C recording infrared spectrophotometer employing a sodium chloride prism. The values for the complete spectra of the ethylenimine ketones, IA, IB, IIA, and IIB given in Table I were obtained by Dr. H. S. Gutowsky and Miss E. M. Petersen of the Department of Chemistry, University of Illinois. The strong bands assignable to the carbonyl stretching vibrations were found at the following wave numbers: for IA, 1685 cm^{-1};IB, 1656 cm^{-1}; IIA, 1681 cm^{-1}; and IIB, 1660 cm^{-1}. Dr. S. F. D. Orr of the Chester Beatty Research Institute, London, England determined the spectra for the remaining compounds of this investigation. The carbonyl bands were found at the following wave numbers: for β,*p*-diphenylpropiophenone (VI), 1675 cm^{-1}; *trans*-4′-phenylchalcone, 1657 cm^{-1}; 1-cyclohexyl-2-(*p*-phenylbenzoyl)ethylenimine (1), 1671 cm^{-1}; and *trans*-epoxybenzylacetophenone, 1687 cm^{-1}. A further study of the infrared spectra of these and other related compounds in various solvents is being carried on at present.

SUMMARY

1. The *cis* and *trans* geometrical isomers of 1-cyclohexyl- and 1-methyl-2-phenyl-3-(*p*-phenylbenzoyl)ethylenimine have been synthesized and separated. Their configurations have been assigned on the basis of their behavior with phenylhydrazine and from the differences observed in their characteristic carbonyl bond absorption bands in the ultraviolet and infrared ranges of the spectrum.

2. A discussion of structural factors effecting hyperconjugation of various three-rings with aryl and aroyl groups based on the absorption spectra studies is given. *Cis*-2-aryl-3-aroylethylenimines show steric inhibition of hyperconjugation. *Trans*-2-aryl-3-aroylethylenimines are found to have considerable conjugated unsaturation which may be ascribed to the ability of the π-electron orbitals of both the 2-aryl and the 3-aroyl groupings to overlap the endocyclic *bent bond* hybridized orbitals of the three-ring. The presence of unsaturated groups on both carbons of the ring arranged *trans* to each other is required if considerable interaction is to take place. The size of the group on nitrogen is of little importance. Analogies to be expected with related epoxyketones and cyclopropyl carbonyl compounds have been pointed out.

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