Studies in Light Absorption. Part XI. Substituted Benzaldehydes, Acetophenones and Related Compounds. The Effects of Steric Conformation on the Electronic Spectra of Conjugated Systems.*

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In conjugated systems X–Y, changes in steric conformation about the single bond can give rise to two types of spectral effects : (1) changes in absorption intensity alone, (2) wavelength displacements of the characteristic electronic bands. Good examples of the first type are provided by alkylated benzaldehydes, acetophenones, cyclic aromatic ketones and related compounds, comprehensive data for which are presented and analysed in detail.

The general discussion of steric effects given previously (Part VI, *J.*, 1949, 1890) is amplified and it is deduced by an application of the Franck–Condon principle that effects of type (1) are produced by transitions between non-planar ground states and uniplanar (or near-planar) excited states, while effects of type (2) are produced by transitions between non-planar ground and excited states. In the former case, the mean interplanar angle θ_1 between X and Y in the ground state is approximately given by $\cos^2 \theta_1 = \varepsilon/\varepsilon_0$, where ε_0 is the absorption coefficient expected for the uniplanar system ($\theta_1 = 0$). The values calculated in this way for the angle between the phenyl and the carbonyl group in *o*-alkylated acetophenones and cyclic aromatic ketones agree well with those deduced from dipole moments and scale models (cf. Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117; Braude, *Experientia*, 1955, in the press).

IN an earlier paper (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, Part VI, *J.*, 1949, 1890), the principal types of steric effect encountered in the electronic spectra of conjugated systems were classified into three main classes according to the structural

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* Part X, *J.*, 1952, 1069.

conditions by which they are produced. One of these relates to changes due to substituents, such as alkyl groups, which normally cause only relatively minor spectral differences in the near-ultraviolet or visible region. The first examples of this class were discovered by Pickett, Walter, and France (*J. Amer. Chem. Soc.*, 1936, **58**, 2296) in the diphenyl series and many analogous cases were subsequently described by Rodebush and his co-workers (*ibid.*, 1940, **62**, 2906; 1941, **63**, 3018; 1946, **68**, 896) and others. Most of the early observations refer to the almost complete disappearance of a band (*K*-band) characteristic of a conjugated system Ph–X on the introduction of two *o*-methyl substituents into the phenyl ring, often accompanied by the appearance of a new band at shorter wavelength. Thus, 2 : 2′ : 6 : 6′-tetramethyldiphenyl, as well as *o*-ditolyl, show practically no trace of the intense band near 2500 Å of the parent compound, diphenyl, but exhibit new bands near 2200 Å (cf. Beaven, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131; Braude and Forbes, *J.*, 1955, 3776). The generally accepted interpretation of this type of steric effect [subsequently referred to as type (2)], resulting in a hypsochromic displacement of a *K*-band, is that the *o*-substituents prevent the adoption by the conjugated system X–Y of the uniplanar, or near-planar, conformation required for maximum electronic interaction between X and Y. The *K*-bands of such systems can usually be ascribed to $N \longrightarrow V$ transitions from essentially homopolar ground states to dipolar excited states in which conventional single bonds possess increased double-bond character (cf. Mulliken, *J. Chem. Phys.*, 1939, **7**, 121). As a result, steric hindrance to uniplanarity raises the energy of the excited state more than that of the ground state, *i.e.*, the transition energy increases and $\lambda_{max.}$ is displaced to shorter wavelength. Thus, steric effects of this type involve transitions between non-planar ground states and non-planar excited states.

Another type of steric effect produced by alkyl substituents and other groups of weak conjugating properties is a reduction in the intensity of a *K*-band, without a significant hypsochromic shift. The existence of this kind of effect [subsequently referred to as type (1)] was first recognised in connection with *cyclo*hexene derivatives (Part VI, *loc. cit.*) and many further examples have accumulated during the last five years (cf. Braude and Jones, *J. Amer. Chem. Soc.*, 1950, **72**, 1041; Turner and Voitle, *ibid.*, 1951, **73**, 1403; Oroshnik, Karmas, and Mebane, *ibid.*, 1952, **74**, 295; Henbest and Woods, *J.*, 1952, 1150; Braude, Bruun, Weedon, and Woods, *J.*, 1952, 1419; Farrer, Hamlet, Henbest, and Jones, *J.*, 1952, 2657). The absence of unusual wavelength displacements means that steric effects of type (1) do not significantly alter the transition energy and, since it is highly unlikely that the ground and the excited state would be affected equally, this implies that the separate energy levels are essentially unchanged. Hence, steric effects of type (1) represent a decrease in transition probability alone. An explanation of such phenomena in general terms was put forward in Part VI; it was suggested that, when steric hindrance to uniplanarity is comparatively weak, the relevant transitions might be restricted to those vibrational states of the molecule in which a sufficient degree of planarity is attained. A more detailed interpretation along these lines is given in the sequel. It will be shown by an application of the Franck–Condon principle that steric effects of type (1) can be explained as arising from transitions between non-planar ground states and uniplanar (or near-planar) excited states and that, on certain assumptions, the mean interplanar angle (θ_1) in the ground state can be deduced from the decrease in ε. The analysis of the data in the alicyclic series is rendered more complex by the fact that the two "*ortho*" (*i.e.*, 2 : 6)-positions in *cyclo*hexene derivatives are not structurally equivalent and by the possible existence of two uniplanar *s-cis-trans*-isomers ($\theta_1 = 0°$ and $180°$) which would be expected to show different light-absorption properties (cf. Braude and Timmons, Part XII, *J.*, 1955, 3766). This complication is absent in the corresponding phenyl derivatives, and although the earlier work of Rodebush and others was not sufficiently extensive to draw a distinction between the two types of steric effect, the available data indicated that effects of type (1) are also common in the aromatic series. This has now been confirmed by a more detailed investigation of *ortho*-substituted benzaldehydes, acetophenones, and related compounds, and it will be shown that the conformations deduced from the spectral properties are in satisfactory agreement with those which can be derived from measurements of dipole moment and from scale models.

Most of the required compounds were either known or accessible by standard methods which are described in the Experimental section. Some marked discrepancies with the literature were noted in the case of 2 : 6-dimethylbenzaldehyde and 2 : 6-dimethylacetophenone. The aldehyde was prepared by the dehydrogenation of the Diels–Alder adduct of piperylene and crotonaldehyde (Holmes *et al.*, *Canad. J. Res.*, 1948, **26**, *B*, 248) and had m. p. 31°, to be compared with m. p. 11° reported by Lock and Schmidt (*J. prakt. Chem.*, 1934, **140**, 229). The structure of the aldehyde was confirmed by oxidation to 2 : 6-dimethylbenzoic acid, which was converted into 2 : 6-dimethylacetophenone by reaction with excess of methyl-lithium. The ketone formed a 2 : 4-dinitrophenylhydrazone under the usual conditions and its spectral properties are quite different from those recently recorded by Schwartzman and Corson (*J. Amer. Chem. Soc.*, 1954, **76**, 784) for a product which did not yield ketonic derivatives.

Benzaldehydes.—Benzaldehyde exhibits three groups of bands near 2400, 2800, and 3300 Å, designated *K*-, *B*-, and *R*-bands, respectively (*Ann. Reports*, 1945, **42**, 105). The high intensity *K*-band is due to an allowed transition of the benzoyl chromophore which may be represented by $\text{Ph–C=O} \longrightarrow {}^{+}\text{Ph=C–O}^{-}$; the other two bands are of low intensity and are ascribed to forbidden transitions associated with the partial phenyl and carbonyl chromophores. Data for a number of alkylated benzaldehydes (Table 1) show that methyl substituents cause only the usual bathochromic displacements; thus the centres of the *K*-bands are shifted by *ca.* 50 Å and those of the *B*-bands by *ca.* 100 Å to longer wavelengths per methyl group, and the *R*-bands consequently become obscured by the falling branch of the *B*-bands. The bathochromic displacements of the *K*-bands can be ascribed to the effects of the methyl group in facilitating the accommodation of the positive charge in the benzenoid ring, either inductively or by hyperconjugation (cf. Bowden and Braude, *J.*, 1952, 1068; Sweeney and Schubert, *J. Amer. Chem. Soc.*, 1954, **76**, 4625; Burawoy and Spinner, *J.*, 1955, 2085) and they are unaccompanied by any *pronounced* changes in intensity.

Closer inspection, however, reveals that while *m*-methyl substituents cause little change on ε, *p*-methyl substituents produce a small increase $(+\Delta\varepsilon \sim 1000)$, no doubt associated with the electromeric interaction which will be much more effective in the *para*- than in the *meta*-position. *o*-Methyl substituents, however, produce a small, but definite, decrease in ε, although from electronic considerations alone they would be expected to have effects similar to those of *p*-methyl substituents. The ratio $(\varepsilon/\varepsilon_0)$ of the observed extinction coefficients to those calculated on the assumption that, in the absence of a special "*ortho*"-effect, *o*-methyl substituents would increase ε by the same amount as *p*-methyl substituents, is 0·86 for *o*-tolualdehyde and shows little further decrease in 2 : 6-dimethyl- and 2 : 4 : 6-trimethyl-benzaldehyde (see Table 3).

TABLE 1. *Ultraviolet-light absorption of alkylated benzaldehydes and their derivatives.*

Ph·CHO derivative	Aldehyde[1]						Semi-carbazone[2]		2 : 4-Dinitro-phenylhydrazone[3]	
	K-Band		*B*-Band		*R*-Band					
	$\lambda_{\text{max.}}$ (Å)	ε	$\lambda_{\text{max.}}$ (Å)	ε	$\lambda_{\text{max.}}$ (Å)	ε	$\lambda_{\text{max.}}$ (Å)	ε	$\lambda_{\text{max.}}$ (Å)	ε
Unsubstd.					3280	57	2810	22,000	3770	28,500[4]
	2420	14,000	2800	1400	3380	53				
	2480	12,500	2890	1200	3530	19				
					3700	6				
p-Me	2510	15,000	2790	1200	3260	30	—	—	—	—
	2570	12,500	*2840*	1000	*3400*	23				
m-Me	2450	13,500	2800	1000	—	—	2840	18,600[5]	—	—
	2510	12,000	2900	800						
o-Me	2430	12,500	2910	1700	3220	45	2810	17,700	3860	30,600
	2510	13,000					2910	17,300		
$2 : 6\text{-Me}_2$ ...	2510	12,500	2990	1900	—	—	2810	17,600	3800	30,800
	2560	11,500	3040	1800	—	—	2910	16,200		
$2 : 4 : 6\text{-Me}_3$	2640	14,500	3000	2100	—	—	2810	18,500	3860	29,500
							2900	17,800		

[1] In *n*-hexane or *cyclo*hexane. Figures in italics represent inflections. [2] In ethanol. [3] In chloroform. [4] Braude and Jones, *J.*, 1945, 498. [5] Data obtained by Mr. R. L. Erskine.

The data for the aldehydes by themselves do not allow any certain interpretation of the *ortho*-effect. It could be suggested that the *ortho*-effect is due to intramolecular hydrogen-bonding between the carbonyl and an *o*-methyl group, as has been inferred from other evidence (cf. Watson, " Modern Theories of Organic Chemistry," Oxford, 1937; Kadesh and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310). Since only one *o*-methyl group could participate in such hydrogen-bonding, this would be compatible with the observation that the " *ortho* "-effect is almost the same with one as with two *o*-methyl groups. On the other hand, hydrogen-bonding involving C–H bonds is known to be very weak, and would not be expected to have any marked influence on ultraviolet-light absorption. Vibrational spectral properties are much more sensitive in this respect, but the available data are also inconclusive. The Raman carbonyl stretching frequencies decrease in the sequence phenylacetaldehyde (1718 cm.$^{-1}$), benzaldehyde (1700 cm.$^{-1}$), *o*-tolualdehyde (1688 cm.$^{-1}$), and mesitylaldehyde (1687 cm.$^{-1}$) (Saunders, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3121); the change in frequency produced by *o*-methyl groups might be due either to increased conjugation (as indicated by the shift in $\lambda_{max.}$, see above), or to hydrogen-bonding, or to both. However, when considered in conjunction with the data for alkylated acetophenones, the small " *ortho* "-effect in the *o*-methyl benzaldehydes seems very probably to be mainly steric in origin and due to a slight obstruction to the coplanar arrangement of the phenyl ring and the formyl group.

Acetophenones.—The ultraviolet absorption of acetophenone is very similar to that of benzaldehyde and the bands can be interpreted in an analogous manner (Table 2). As before, alkyl groups in any of the three ring-positions cause only the normal bathochromic displacements, which are accompanied for *p*-substituents by a small increase in the intensities of the *K*-band ($+\Delta\varepsilon \sim 1500$). In contrast to results with the benzaldehydes, however, *o*-methyl substituents produce very marked hypochromic effects, with ratios of observed to expected values ($\varepsilon/\varepsilon_0$) ranging from 0·9 to 0·2 (see Table 3). From the fact that the observed intensities of the *K*-bands of acetophenone and 2 : 4-dimethylacetophenone are almost equal, whereas in 2 : 4 : 6-trimethylacetophenone the intensity is reduced to about one-quarter, O'Shaughnessy and Rodebush (*ibid.*, 1940, **62**, 2906) concluded that *two* *o*-methyl substituents are required to produce the effect. The present, more extensive data show, however, that the spectral properties of 2 : 4-dimethylacetophenone are, in fact, somewhat exceptional and that in 2-methyl- and 2 : 5-dimethyl-acetophenone one methyl substituent is sufficient to decrease ε to about half of the expected value ($\varepsilon/\varepsilon_0$ = 0·58 and 0·66). Actually, 2 : 4-dimethylacetophenone also shows a definite, though smaller, *ortho*-effect, but this only becomes apparent when the increments in ε normally expected for the two methyl substituents are taken into account ($\varepsilon/\varepsilon_0$ = 0·85).

TABLE 2. *Ultraviolet-light absorption of alkylated acetophenones and their derivatives.*

	Ketone[1]						Semi-carbazone[2]		2 : 4-Dinitrophenyl-hydrazone[3]	
Ph·COMe derivative	*K*-Band		*B*-Band		*R*-Band					
	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
Unsubstd.	2430	13,200	2790	1200	*3150*	55	2700	20,400	3800	27,500[4]
							2780	17,700		
4-Me	2520	15,100	—	—	—	—	2750	19,900[5]	—	—
2-Me	2420	8700	2810	1200	*3310*	50	2450	11,800	3660	21,400[6]
	2450	8300					2500	12,200		
							2560	11,800		
2-Bu^n	2420	8100	2820	1100	—	—	2450	11,700	3680	23,900[6]
	2450	7600	2910	1000						
2 : 4-Me$_2$ ...	2510	14,100	2820	1700	—	—	—	—	3720	24,900
	2560	12,300	2910	1300						
2 : 5-Me$_2$ ...	2450	9900	2960	1800	—	—	—	—	3690	26,700
	2510	8700								
2 : 6-Me$_2$ ...	2510	5600	*2810*	890	—	—	—	—	3600	28,900
	2560	5200	*2900*	740						
2 : 4 : 6-Me$_3$	2420	3600[7]	2800	400	—	—	—	—	—	—

[1] In ethanol. [2] In ethanol. [3] In chloroform. [4] Braude and Jones, *J.*, 1945, 498. [5] Turner and Voitle, *J. Amer. Chem. Soc.*, 1951, **73**, 1403. [6] Braude, Jones, Sondheimer, and Toogood, *J.*, 1949, 607. [7] O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906.

The observation that a strong *ortho*-effect is exhibited by acetophenones containing only a single *o*-alkyl substituent supports the conclusion reached above, that intramolecular hydrogen-bonding plays no significant part in these phenomena. If it did, it would be expected that *o*-tolualdehyde and *o*-methylacetophenone would assume the conformations (I*b*) and (III*a*) respectively, and that any resulting spectral abnormality would be the same in both.* The only plausible prime cause of the much larger *ortho*-effect found with the ketones is the large increase in steric hindrance to uniplanarity of the Ph–C=O chromophore when the formyl group is replaced by an acetyl group. This increase can be clearly seen by comparing the projections of the two less-hindered conformations (I*a*) and (III*a*) which show overlap in the ketone but not in the aldehyde, on the basis of the dimensions chosen.

At this point, the choice of radii for scale diagrams requires discussion. In Part VI (*loc. cit.*) the use of covalent in place of the customary van der Waals radii was adopted and briefly justified on the grounds that covalent radii represent a reliable ***minimum*** measure of interference radii between non-bonded atoms belonging to the same molecule, whereas van der Waals radii would predict marked steric effects in many compounds, the ultraviolet-light absorption properties of which are normal. Thus, for example, considerable overlap occurs in acetophenone itself, on the basis of van der Waals radii, between the acetyl group and the *o*-hydrogen atoms, whereas the close similarity between the *K*-bands of benzaldehyde and acetophenone indicates the absence of spectroscopically detectable steric effect in the unsubstituted ketone (cf. footnote, below*). That van der Waals radii are an excessive measure of atomic size even in connection with the stability of optical isomers is apparent from calculations by Stanley and Adams (*J. Amer. Chem. Soc.*, 1930, **52**, 1200). Discussion with several colleagues has shown, however, that our earlier statement that " it is now generally accepted that van der Waals radii represent too large a measure of the intramolecular interference properties of atoms " was not entirely justified. Now, since the repulsion energy between non-bonded atoms is a highly exponential function of distance, the choice of a suitable scale of interference radii is mainly a matter of convenience and will depend on the physical property under investigation. Absorption of ultraviolet light corresponds to energy increments of the order of 100 kcal./mole and the smallest wavelength displacements (*ca.* 50 Å) which are significant in the electronic spectra of organic compounds in solution correspond to energy differences of *ca.* 2 kcal./mole. Thus, ultraviolet-light absorption will be a less sensitive index of steric effects than, for instance, reaction rates where differences of *ca.* 0·1 kcal./mole will be detectable, but a more sensitive index than the existence of isolable optical isomers which requires energy barriers of *ca.* 15 kcal./mole. Now, potential-energy curves for a number of atom pairs (cf. Evans, *Trans. Faraday Soc.*, 1946, **42**, 741; Hill, *J. Chem. Phys.*, 1948, **16**, 399) show that interpenetration energies of the order of 1—3 kcal./mole correspond to distances of approach of about 1 Å less than the sum of the van der Waals radii, a value which is close to the difference between van der Waals and covalent radii. Thus, if no overlap occurs on the basis of covalent radii, steric repulsion will normally amount to less than 3 kcal./mole. Clearly the precise value in any particular case will depend closely on the shape of the potential energy curves concerned and the onset of spectrally detectable steric effects will occur somewhere between the van der Waals and the covalent distances. For the present purpose, it has now been found suitable to represent interference radii as *twice* the covalent radii, *i.e.*, 0·60 Å for hydrogen, 1·70 Å for methyl, and 1·1 Å for doubly bonded oxygen. These values are about *half* the van der Waals radii. (A slightly larger value, 0·75 Å, for hydrogen has been advocated for general purposes by Crombie, *Quart. Rev.*, 1952, **6**, 101.) It will be noted that, with the dimensions chosen, an *o*-methyl group causes no steric overlap with the hydrogen atom of a formyl group, slight overlap with the oxygen atom of a formyl or acetyl group, and considerable overlap with the methyl portion of an acetyl group [See projection (I)—(III)].

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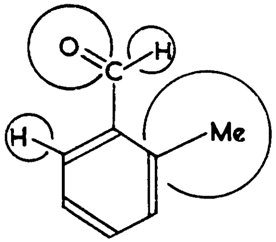
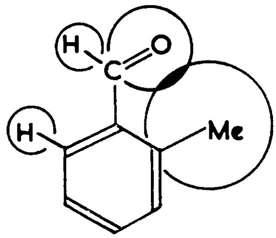
* It might be argued that difference arises from steric interference between the acetyl-methyl group and the *o*-hydrogen atom. If such interference existed, it would be expected to operate also in the parent compound, acetophenone, compared with benzaldehyde, whereas the intensities of the *K*-bands are here almost identical. It is partly on this basis that the interference radii have been so chosen as to show no overlap in acetophenone itself.

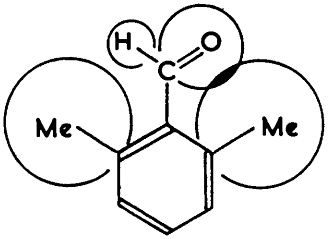
We now return to the main theme. The projection diagrams (I) and (III) indicate that *o*-tolualdehyde and 2-methylacetophenone can assume conformations in which the benzene ring and the carbonyl group are essentially coplanar at the expense of less than *ca.* 3 kcal./mole to overcome steric hindrance. In 2 : 6-dimethylacetophenone (IV) the acetyl-methyl and one of the *o*-methyl groups must overlap, but if the hydrogen atoms were shown separately instead of the solid methyl groups it would be seen that even in this case covalent overlap is comparatively small and the same must obviously be true for all the other aldehydes and ketones in Tables 1 and 2. Hence, whatever the degree of uniplanarity which has to be attained in either the ground or the excited state of the transition $\mathrm{Ph{-}C{=}O} \longrightarrow {}^{+}\mathrm{Ph{=}C{-}O}^{-}$, any increase in transition energy due to the steric effect of *o*-alkyl substituents will be rather *less* than 3 kcal./mole. No significant hypsochromic wavelength displacements of the *K*-band would therefore be expected, and none are found. The alkylated acetophenones, like their acyclic analogues (Part VI), thus provide an excellent example of relatively weak steric hindrance to uniplanarity which does not result in any appreciable change in $\lambda_{\mathrm{max.}}$, and yet results in a marked decrease in $\varepsilon_{\mathrm{max.}}$.



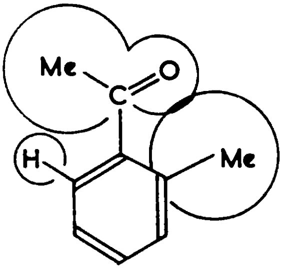
(I*a*)



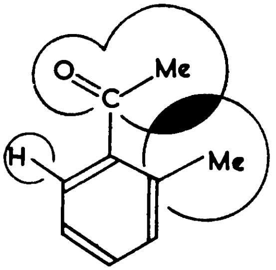
(I*b*)



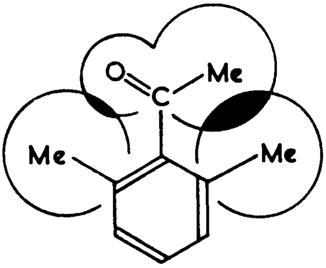
(II)



(III*a*)



(III*b*)



(IV)

The absorption intensity is determined by the transition probability which, in turn, is governed by three things: (i) the selection rules, (ii) the transition moment, which is related to the change in dipole moment in passing from the ground to the excited state; and (iii) the chromophore area (cf. Braude, *J.*, 1950, 379). A steric effect on ε without change in λ cannot be due to a reduction in transition moment, for an $\varepsilon/\varepsilon_0$ ratio of 0·5 or less would then require a highly non-planar excited state, which, as discussed on p. 3755, would in turn be expected to lead to an appreciable change in transition energy. The effective chromophore area will also be little altered by a change in interplanar angle. This leaves only the transition probability, *i.e.*, a change in selection rules resulting in a reduced " allowedness " of the transition, as a likely cause of the decrease in ε. Such a change could come about in the following way (the principle is general though it will be illutrated in terms of the Ph·CO·R system). The upper limit of about 3 kcal./mole deduced for the energy parameter of the steric effect is considerably greater than the spacings of the energy levels of the torsional vibration about the Ph–CO axis of a molecule such as acetophenone. In an *ortho*-substituted, sterically hindered acetophenone, the mean (equilibrium) angle between the planes of the phenyl and the carbonyl group in the ground electronic state will have some value θ_1 between 0° and 90°, but even at room temperature higher torsional levels corresponding to smaller values of θ will be populated. In the excited electronic state, the mean interplanar angle will have some value θ_2, which will be considerably smaller than θ_1 since the double-bond character of the Ph–CO link is greatly increased. Now, since the motion of electrons is very much faster than that of atomic nuclei (the Franck–Condon principle), the actual angle θ in any individual molecule cannot change during an electronic transition and only those molecules in which $\theta \sim \theta_2$ will be able to undergo the transition (see Fig. 1). The fraction r of all molecules fulfilling this condition will be some function of $(\theta_1 - \theta_2)$. The simplest function which passes through the fixed points ($\Delta\theta = 0°, r = 1$; $\Delta\theta = 90°, r = 0$; $\Delta\theta = 180°, r = 1$) is $\cos^2(\theta_1 - \theta_2)$. Since the fraction r will also be approximately equal to $\varepsilon/\varepsilon_0$, we have : *

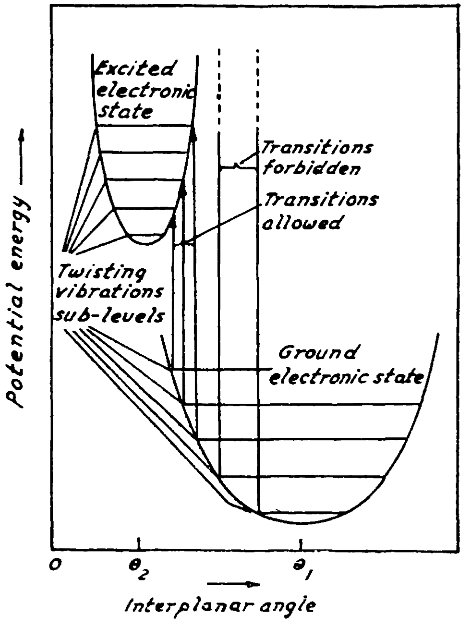
$$\varepsilon/\varepsilon_0 = \cos^2(\theta_1 - \theta_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or, if we make the additional assumption (which will be justified later) that $\theta_2 \sim 0°$,

$$\varepsilon/\varepsilon_0 = \cos^2 \theta_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The interplanar angles for the electronic ground states derived in this way for *ortho*-alkylated benzaldehydes and acetophenones are given in Table 3 which shows that in the aldehydes, the angle is *ca.* 20° in the presence of either one or two *o*-methyl groups, while in the ketones the angle is *ca.* 35° in the presence of one, and *ca.* 60° in the presence of two, *o*-methyl groups, and that the *actual* values of θ_1 are also somewhat dependent on *meta*- and *para*-substituents.

FIG. 1. *Schematic representation of electronic transitions between a non-planar ground electronic state and a near-planar excited electronic state.*



If these conclusions are correct, they should be confirmed by other physical properties which are influenced by resonance interaction but are conditioned by the electronic ground states alone. Two such properties are vibrational spectra and dipole moments. Only fragmentary data are available for the former, but the Raman carbonyl stretching frequencies of the ketones, in contrast to those of the aldehydes (see above), are increased by *ortho*-alkylation (acetophenone, $\nu = 1684$ cm.$^{-1}$; acetylmesitylene, $\nu = 1699$ cm.$^{-1}$; Sanders *et al.*, *loc. cit.*), indicating that in the ketones the de-coupling effect of the substituents outweighs their conjugative effects. (A detailed study of the infrared spectra, which may be expected to yield more diagnostic information, is being undertaken in these laboratories by Mr. R. L. Erskine.) More extensive data are available on dipole moments (Kadesh and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310; Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957; Le Fèvre and Le Fèvre, *J.*, 1950, 1829; Smith, *J.*, 1953, 109). Smith compared the moments of benzaldehyde ($\mu = 2{\cdot}92$ D) and mesitaldehyde ($\mu = 2{\cdot}96$ D) and concluded that there was little or no steric hindrance in the latter, in agreement with the present evidence. The various measurements on acetophenones are not in very

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* More precisely, the ratios of the integrated band areas should be used rather than $\varepsilon/\varepsilon_0$. However, the band widths are not markedly affected by alkyl substitution, so that the ratios are not appreciably different.

good agreement, perhaps partly owing to different methods of evaluation, and we shall use the values obtained by Sutton and his co-workers, which are the most complete. In Table 3, the observed dipole moments are given, together with those calculated (μ_0) for the coplanar conformations on the following basis: (i) the moments of methylacetophenones are compounded of the group moments of C=O (taken as 2·96, the value for acetophenone) and C_6H_4–Me (taken as 0·40, the value for toluene, for *o*- and *m*-methyl substituents, and as 0·54, the observed vector component in 4-methylacetophenone, for *p*-methyl substituents); (ii) the vector addition is carried out assuming the carbon–carbon and carbon–oxygen bond angles to be 120°; (iii) for the unsymmetrically substituted ketones, only the less-hindered coplanar conformation is taken into account. The interplanar angle θ_1 can then be expressed by

$$\cos^2 \theta \sim (\mu_{\text{obs.}} - \mu_{90})/(\mu_0 - \mu_{90}) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where μ_{90} is the moment for the completely deconjugated system in which the planes of the phenyl and the carbonyl group are at right angles and which can be taken to be the same as that of a saturated ketone (*i.e.*, $\mu_{90} = 2{\cdot}75$, the value for acetone). Table 3 shows that, except for 2 : 4-dimethylacetophenone, the interplanar angles θ_1 derived in this way from spectral and dipole-moment data are in fair agreement. The agreement is, in fact, as good as could be expected in view of the approximations made and of the fact that expression (3) is very sensitive to uncertainties in μ. Our evaluation of the dipole moment evidence differs in some respects from that of Bentley *et al.* (*loc. cit.*) who employed a slightly different method of estimating μ_0 and, partly on the basis of the abnormal moment exhibited by 2 : 4-dimethylacetophenone, concluded that "a single methyl group is not sufficient to prevent conjugation."

TABLE 3. *Steric effects in* ortho-*alkylated benzaldehydes and acetophonones.*

Benzaldehyde derivative	$\varepsilon/\varepsilon_0$ [a]	θ_1 [b]	$\mu_{\text{obs.}}$ [c]	μ_0 [d]	θ_1 [e]	Acetophenone derivative	$\varepsilon/\varepsilon_0$ [a]	θ_1 [b]	$\mu_{\text{obs.}}$ [c]	μ_0 [d]	θ_1 [e]
Unsubstituted	1·00	0°	2·92	2·92	0°	Unsubstituted	1·00	0°	2·96	2·96	0°
o-Me	0·86	21	—	—	—	2-Me	0·58	40	2·62	2·56	34
2 : 6-Me_2.........	0·78	28	—	—	—	2 : 4-Me_2	0·85	24	2·95	2·83	—
2 : 4 : 6-Me_3 ...	0·85	22	2·96	2·99	15	2 : 5-Me_2	0·66	35	2·85	2·96	46
						2 : 6-Me_2	0·34	55	—	—	—
						2 : 4 : 6-Me_3 ...	0·20 [*]	63	2·81	3·03	62

[a] Ratio of observed ε of *K*-band to that expected for uniplanar system. [b] Interplanar angle calculated from ε by equation (2). [c] Observed dipole moment (D) in benzene solution (Bentley *et al.*, and Smith, *locc. cit.*). We are indebted to Dr. T. W. Smith for kindly determining and allowing us to quote the value for 2-methylacetophenone. [d] Dipole moment expected for uniplanar system. [e] Interplanar angle calculated from μ by equation (3).

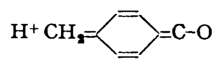
[*] A lower value of ε (2500) has recently been reported for 95% ethanol (Schubert, Sweeney, and Latovrette, *J. Amer. Chem. Soc.*, 1954, **76**, 5462). This gives $\varepsilon/\varepsilon_0 = 0{\cdot}14$ and $\theta_1 = 67°$.

In deducing the simplified expression (2) for the relation between ε and the ground-state interplanar angle θ_1, the assumption was made that the excited state interplanar angle θ_2 is almost zero. This assumption is supported by the fair agreement between the values of θ_1 calculated from the spectral data and from the dipole moment, which is a property of the electronic ground state alone. If the more accurate expression (1) is used, the "spectroscopic" angle actually represents ($\theta_1 - \theta_2$) and the differences between the second and the fifth column of figures in Table 3 therefore give θ_2. These differences are 6° for 2-methylacetophenone, 11° for 2 : 5-dimethylacetophenone, and 1° for 2 : 4 : 6-trimethylacetophenone, so that θ_2, is, in fact, quite small.

Although, for reasons already discussed, no precise relationship is to be expected between θ_1 and the amount of steric overlap in the planar conformations as indicated by models or scale diagrams, at least a semi-quantitative connection does exist. The rapid increase in overlap in the sequence (*o*-Me : –C–H; negligible) < (*o*-Me : –C=O; slight) < (*o*-Me : –C–Me; marked) explains why, in benzaldehyde, the effect of two *o*-methyl groups is hardly greater than that of one, while in acetophenone the effect is enhanced by a second *o*-methyl group, though not nearly doubled. It is noteworthy that the extent of overlap indicated in the conformation (III*a*) of *o*-methylacetophenone is almost the same as in the planar conformation of 2 : 6-dimethylbenzaldehyde (II); yet the spectral effect in the mono-*ortho*-alkylated ketone is considerably greater than in the di-*ortho*-alkylated aldehyde. It is possible that, owing to the electron-repelling influence of a methyl group, the effective interference radius of the oxygen atom is, in fact, somewhat larger in an acetyl than in a formyl group and that this accounts for the difference. It also suggests, however, that an appreciable fraction of the molecules of 2-methylacetophenone in the ground state have non-coplanar conformations approaching the more hindered conformation (III*b*) while others have the less-hindered conformation (III*a*), *i.e.*, that the energy levels are sufficiently close for vibrational states with θ_1 differing by 90° to be significantly populated.

The fact that an *o*-butyl group has only a slightly larger effect than an *o*-methyl group (Table 2) is understandable, since all but the first methylene group of the alkyl side chain can assume conformations such that little additional interference is caused. Data for 2-hydroxyacetophenone ($\lambda_{max.}$ 2560 Å, ε 10,500; Morton and Stubbs, *J.*, 1940, 1347; Valyashko and Rozum, *J. Gen. Chem. Russia*, 1946, **16**, 593; 1947, **17**, 755; Dannenberg, *Z. Naturforsch.*, 1949, **4b**, 327) and 2 : 6-dihydroxyacetophenone ($\lambda_{max.}$ 2630 Å, ε 8300; Cram and Cranz, *J. Amer. Chem. Soc.*, 1950, **72**, 595) show that *o*-hydroxyl groups also produce the expected steric reduction in intensity, accompanied by the rather larger bathochromic shifts usual for such substituents (Bowden, Braude, and Jones, *J.*, 1946, 948; Bowden and Braude, *J.*, 1952, 1068). Hydrogen-bonding no doubt also comes into play in this case and accounts, at least in part, for the large spectral differences between the hydroxyl- and methoxyl-substituted ketones (cf. Cram and Cranz, *loc. cit.*). The correlation also holds fairly well when the conjugating group rather than the hindering *o*-substituent is varied (see below). A similar correlation has been noted previously for *ortho*-substituted dialkylanilines by Klevens and Platt (*J. Amer. Chem. Soc.*, 1949, **71**, 1714) who carred out the reverse procedure from that followed here and compared the reductions in absorption intensities (expressed as oscillator strengths) with the interplanar angles deduced from scale models.

Lastly, the rather unexpected influence of *p*-methyl substituents on the magnitude of the *ortho*-effect (see Table 3) deserve comment. In 2 : 4 : 6-trimethylbenzaldehyde and 2 : 4-dimethylacetophenone the *p*-methyl group reduces the *ortho*-effect, whereas in 2 : 4 : 6-trimethylacetophenone it enhances it. A tentative interpretation of these second-order effects is as follows. The mesomeric effect of a methyl group in the *para*-position will, in itself, promote the uniplanarity of the conjugated system owing to the contributions from hyperconjugated structures such as that inset. In 2 : 4 : 6-trimethylbenzaldehyde where the steric obstruction to uniplanarity is quite weak, the interplanar angle is therefore reduced as compared with 2 : 6-dimethylbenzaldehyde. Again, in 2 : 4-dimethylacetophenone the system has the choice of one conformation [corresponding to (III*a*)] in which steric hindrance is weak, and a higher proportion of molecules will approach this conformation rather than the more highly hindered (III*b*) in 2-methylacetophenone. In 2 : 4 : 6-trimethylacetophenone, however, both possible uniplanar conformations are equally hindered, and the additional conjugation merely enhances the congestion at the acetyl group, as compared with 2 : 6-dimethylacetophenone. It may be noted that a 5-methyl group has only a negligible influence on θ in accordance with the fact that the mesomeric effect is only very weakly relayed from the *meta*-position.



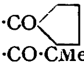
Semicarbazones and 2 : 4-Dinitrophenylhydrazones.—Data for these derivatives are included in Tables 1 and 2. As with the parent carbonyl compounds, there is a marked contrast between the effects of *o*-methyl substituents on the characteristic ultraviolet-absorption bands of the aldehydes and ketones. The benzaldehyde derivatives exhibit essentially normal absorption, and methyl substituents produce only the usual, small bathochromic displacements without significant decreases in intensity. This indicates that the interference properties of the –CH=O and –CH=NX [X = NH·CO·NH$_2$ or NH·C$_6$H$_3$(NO$_2$)$_2$] groups are similar, as would be expected since the covalent radius of nitrogen is slightly smaller than that of oxygen, and since X will lie outside the action radius, at least in the *anti*-stereoisomers (cf. Ramirez and Kirby, *J. Amer. Chem. Soc.*, 1954, **76**, 1037).

The acetophenone derivatives, on the other hand, exhibit markedly abnormal absorption when *o*-methyl substituents are present, but, unlike those for the parent ketones, the bands are displaced to shorter wavelengths as well as decreased in intensity. Thus, the semicarbazone of 2-methylacetophenone has a multiple band located about midway between those of the semicarbazones of acetophenone and of a saturated ketone (cf. $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, $\lambda_{max.}$ 2320 Å) and of about half the intensity; and the absorption of the 2 : 4-dinitrophenylhydrazone is typical of that of a saturated ketone (cf. Braude and Jones, *J.*, 1945, 498). Similar observations have been made with oximes and other derivatives by Grammaticakis (*Bull. Soc. chim. France*, 1940, 527; 1947, 664; 1950, 504; *Compt. rend.*, 1950, **231**, 278) and Ramart-Lucas, Hoch, and Vial (*Bull. Soc. chim. France*, 1952, 220; Ramart-Lucas and Hoch, *ibid.*, p. 422). The hypso- and the hypo-chromic effects undoubtedly have the same cause, and the spectral consequences of steric inhibition to coplanarity are evidently different in the ketones and in their derivatives. These observations are analogous to those made with acetyl*cyclo*hexenes and their derivatives (Part VI) and can be interpreted on the basis of the concept of "partial chromophores." In molecules in which the interplanar angle between the Ph– and the –CMe=O or –CMe=NX group is too large to allow the transition characteristic of the full conjugated system, transitions associated with the partial chromophores will have increased probability. If θ reached the maximum value of 90°, partial chromophore bands would have intensities similar to those in systems containing only the separate groups and the absorption would be approximately additive. Now, in the ketones the strong bands expected for the partial –Ph and –CMe=O chromophore are much less intense than the *K*-bands and are at much shorter wavelengths (~2000 Å; cf. Braude, *Ann. Reports*, 1945, **42**, 105), outside the present range of measurements. In the semicarbazones, on the other hand, and particularly in the 2 : 4-dinitrophenylhydrazones, the bands of the full chromophores $Ar{\cdot}CMe{=}N{\cdot}X$ and of the partial chromophores –CMe=NX are of similar intensity and closer together. Thus the multiple band exhibited by the semicarbazone of 2-methylacetophenone (in which, as in the ketone, about half of the molecules in the ground state will have an interplanar angle greater than the critical value) is to be regarded as a superposition of the full and the partial chromophore bands ($\lambda_{max.}$ *ca.* 2700 and 2300 Å) each having about half their usual intensity. In the 2 : 4-dinitrophenylhydrazones, the reversion of the absorption to the partial chromophore type is more complete and it is possible that, owing to the closer proximity of energy levels in these systems, true resonance degeneracy occurs rather than purely geometrical superposition.

Alkyl Phenyl Ketones and Cyclic Aromatic Ketones.—The principles outlined in the previous sections are equally applicable to alkyl phenyl ketones and cyclic aromatic ketones and their derivatives which have been studied particularly by Ramart-Lucas and her school (Ramart-Lucas and Hoch, *Bull. Soc. chim. France*, 1936, 918; 1938, 848, 1001; 1952, 422; Grammaticakis, *ibid.*, 1940, 527; 1941, 427; Biquard, *ibid.*, p. 55; Ramart-Lucas, Hoch, and Vial, *ibid.*, 1952, 220) (Table 4). The absorptions of propiophenone (V) and butyrophenone are almost identical with that of acetophenone and only a slight reduction in ε is noticeable in secondary alkyl phenyl ketones, such as *iso*butyrophenone (VI) and *cyclo*pentyl phenyl ketone; no appreciable hindrance to uniplanarity is expected in any of these cases since the primary or secondary alkyl group can adopt conformations such that they do not interfere with the *o*-hydrogen atom of the phenyl ring. A radically different situation obtains with *tert.*-alkyl phenyl ketones where at least one of the branch-groups must overlap with the *o*-hydrogen atom if the conjugated Ph–C=O system is to be uniplanar. Hence, *tert.*-butyl phenyl ketone (VII) shows a very marked *ortho*-effect and the calculated interplanar angle θ_1 in the ground state is very similar to that deduced previously for *o*-methylacetophenone. The *ortho*-effect increases only slightly in going from *tert.*-butyl to 1 : 1-dimethylpropyl and 1-ethyl-1-methylpropyl phenyl ketone; as with homologous *ortho*-substituents (cf. 2-butylacetophenone) the mere lengthening of an alkyl chain causes only slight extra hindrance since the additional methylene groups can adopt almost non-hindering conformations.

We now turn to the cyclic ketones. The *K*-bands of indanone, tetralone, and related ketones are almost the same, with respect to both $\lambda_{max.}$ and ε, as that of acetophenone, indicating the the five- and six-membered alicyclic rings permit the carbonyl group to be nearly coplanar with the benzene ring, in agreement with scale models. In benzo*cyclo*hepten-3-one and benzo*cyclo*octen-3-one, however, there is a marked decrease in ε without significant shift in $\lambda_{max.}$ and the interplanar angles calculated by equation (2) are about 40°.

TABLE 4. *Ultraviolet-light absorption and steric effects in alkyl phenyl ketones and cyclic aromatic ketones.**

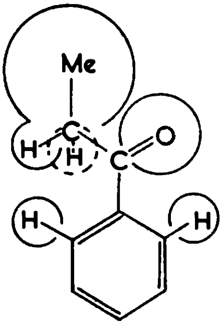
	$\lambda_{max.}$ (Å)	ε	$\varepsilon/\varepsilon_0$	θ_1
Ph·COMe [1]	2420	13,200	1·0	0°
Ph·COEt [1]	2420	13,500	1·0	0
Ph·CO  [2]	2380	12,000	0·89	19
Ph·CO·CMe$_3$ [3, 4]	2420	9,100	0·68	34
Ph·CO·CMe$_2$Et [5]	2390	8,300	0·62	38
Ph·CO·CMeEt$_2$ [5]	2380	7,100	0·53	43
Indanone [3, 4]	2430	12,300	0·91	17
1-Tetralone [3, 4]	2480	11,600 †	0·86	22
1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-9-oxophenanthrene [6]	2490	11,800	0·87	21
Benzo*cyclo*hepten-3-one [7]	2460	8,100	0·60	39
3 : 4-Benzo-1 : 2-*cyclo*hexano*cyclo*hepten-5-one [6]	2470	7,700	0·57	40
Benzo*cyclo*octen-3-one [4, 7, 8]	2470	6,500	0·48	46
Benzo*cyclo*decen-3-one [8]	2560	11,200	0·85	23

* Most of the data refer to ethanol solutions.

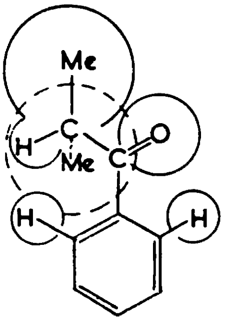
† A lower value (ε 9300) has recently been reported for 95% EtOH (Beyerman, *Rec. Trav. chim.*, 1953, **72**, 550). This would correspond to θ_1 = 34°.

[1] Present work. [2] Braude and Forbes, *J.*, 1951, 1755; Mariella and Raube, *J. Amer. Chem. Soc.*, 1952, **74**, 521. [3] Ramart-Lucas, Hoch, and Vial, *Bull. Soc. chim.*, France, 1952, 220. [4] Heddon and Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 3744. [5] Cram and Knight, *ibid.*, 1952, **74**, 5840. [6] Gutsche and Seligman, *ibid.*, 1953, **75**, 2579. [7] Huisgen and Rapp, *Chem. Ber.*, 1952, **85**, 826. [8] Schubert, Sweeney, and Latovrette, *J. Amer. Chem. Soc.*, 1954, **76**, 5462.

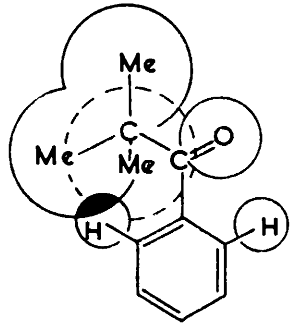
The non-coplanarity here is obviously not due to crowding at the carbonyl function in the same sense as with the open-chain ketones, but is to be ascribed to the effect of the conformation of the alicyclic ring. It can readily be seen with the aid of models that in order that the chain of methylene groups may take up the preferred, staggered zig-zag conformation, the plane of the carbonyl group must be turned out of the plane of the benzene ring, whereas



(V)



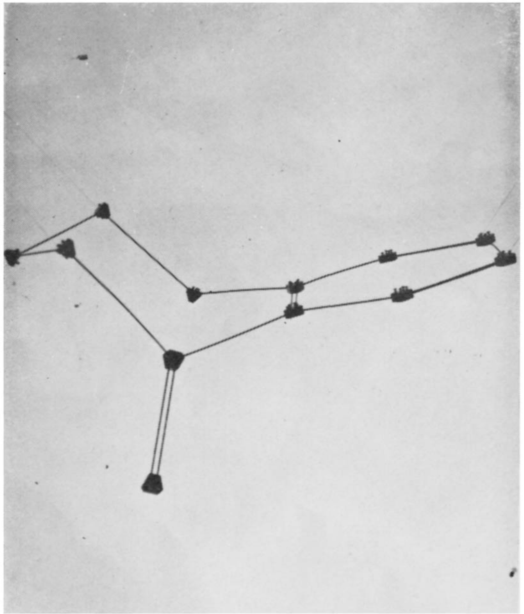
(VI)



(VII)

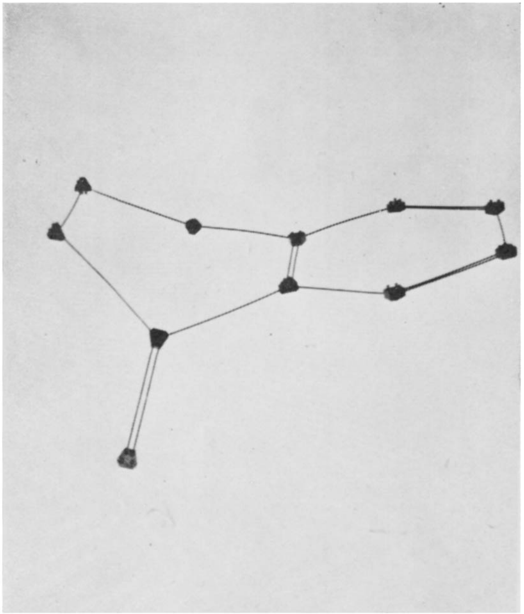
if the chromophore is to achieve uniplanarity, at least one " opposed " conformation must be introduced into the C_4- or C_5-chain. Now, the energy difference between the two corresponding conformations, for example, *n*-butane, is known to be of the same order (3·6 kcal./mole; Pitzer, *Chem. Rev.*, 1940, **27**, 39; Beckett, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488; cf. Turner, *ibid.*, 1952, **74**, 2118) as the Ph–C=O resonance energy, only part of which will, in any case, be lost through non-planarity. It is therefore not surprising that the conformational preference of the alkyl chain prevails over that of the conjugated Ph–C=O system in determining the conformation of the whole molecule. The scale models devised by Barton, which are particularly suitable for this type of problem, indicate (Figs. 2 and 3) that the minimum angles which can be reached in α-tetralone and

FIG. 2.



*Scale model of benzo*cyclo*hexen-3-one (α-tetralone).*

FIG. 3.



*Scale model of benzo*cyclo*hepten-3-one.*

[*To face p.* 3764.

in benzo*cyclo*hepten-3-one between the phenyl ring and the carbonyl group without undue distortion of the staggered alicyclic ring are about 20° and 40° respectively, in remarkably good agreement with the values of 22° and 39° deduced from the spectroscopic data.

EXPERIMENTAL

Light absorptions were determined with a Hilger-Spekker instrument (Part I, *J.*, 1945, 490). Aldehydes were measured in *n*-hexane; in ethanol, rapid hemiacetal formation occurs even at room temperature. Solutions of acetophenones in ethanol, on the other hand, appear quite stable.

Benzaldehyde had b. p. 179°/769 mm., n_D^{21} 1·5468 (semicarbazone, m. p. 223°). *o*-Tolualdehyde (Law and Perkin, *J.*, 1907, **91**, 258) had b. p. 84—85°/17 mm., n_D^{16} 1·5498 (semicarbazone, m. p. 207—208°; 2 : 4-dinitrophenylhydrazone, m. p. 192—193°). *m*-Tolualdehyde had b. p 83°/16 mm., n_D^{23} 1·5401 (semicarbazone, m. p. 216°). Acetophenone had b. p. 90°/25 mm., n_D^{24} 1·5316 (semicarbazone, m. p. 201°). *p*-Methylacetophenone had b. p. 110°/14 mm., n_D^{21} 1·5531. 2 : 4-Dimethylacetophenone, prepared from *m*-xylene and acetyl chloride (Freund and Fleischer, *Annalen*, 1918, **414**, 5), had b. p. 122—123°/27 mm., n_D^{24} 1·5319 [2 : 4-dinitrophenylhydrazone, m. p. 174° (Norris and Arthur, *J. Amer. Chem. Soc.*, 1940, **62**, 874 give m. p. 174—175°)]. 2 : 5-Dimethylacetophenone, prepared from *p*-xylene and acetyl chloride (Freund and Fleischer, *loc. cit.*) had b. p. 52°/0·1 mm., n_D^{22} 1·5290 [2 : 4-dinitrophenylhydrazone, m. p. 173° (Norris and Arthur, *loc. cit.*, give m. p. 174—175°)].

2 : 6-*Dimethylbenzaldehyde*.—An intimate mixture of 4-formyl-3 : 5-dimethyl*cyclo*hexene (8 g.) (Holmes, Alcock, Demianow, Robinson, Rooney, and Sunberg, *Canad. J. Res.*, 1948, **26**, *B*, 248) and sulphur (4·0 g.) was heated to 280° (bath) under reflux in nitrogen for 12 min.; the vigorous evolution of hydrogen sulphide had then ceased. The once distilled, crude product (5·0 g.) was combined with that (5·8 g.) of a second run and fractionated in nitrogen, giving 2 : 6-dimethylbenzaldehyde, b. p. 230°/762 mm., 118°/27 mm., n_D^{18} 1·548. After crystallisation from pentane (once) and methanol (twice) it was obtained in long needles, m. p. 30—31° (Lock and Schmidt, *J. prakt. Chem.*, 1934, **140**, 229, give b. p. 226°/742 mm., m. p. 11°). The semicarbazone, the formation of which required heating on the steam-bath, crystallised from aqueous methanol as plates, m. p. 167—168° (Lock and Schmidt, *loc. cit.*, give m. p. 158°). The 2 : 4-*dinitrophenylhydrazone* crystallised from dilute ethyl acetate solution as red needles, m. p. 250—251° (Found: C, 57·6; H, 4·85; N, 18·1. $C_{15}H_{14}O_4N_4$ requires C, 57·3; H, 4·5; N, 17·85).

An attempted dehydrogenation of 3-formyl-2 : 6-dimethyl*cyclo*hexene with chloranil in boiling xylene (cf. Bowden and Jones, *J.*, 1946, 52) gave only polymeric material. The structure of the aldehyde was confirmed by oxidation. Potassium hydroxide (2·9 g.) in water (8 ml.) was added, with shaking, to a solution of 2 : 6-dimethylbenzaldehyde (0·90 g.) and silver nitrate (5·3 g.) in water (8 ml.) and ethanol (1·6 ml.). The mixture was heated under reflux on the steam-bath for 30 min. with occasional shaking. After cooling and filtering, the combined filtrates and aqueous washings were acidified and extracted with ether. The ethereal extract was dried (Na_2SO_4) and evaporated, giving crude, solid 2 : 6-dimethylbenzoic acid (0·71 g.), which after sublimation at 20 mm. and crystallisation from water formed needles, m. p. 114—115° (Hufferd and Noyes, *J. Amer. Chem. Soc.*, 1921, **43**, 925, give m. p. 116°).

2 : 4 : 6-*Trimethylbenzaldehyde*.—This was prepared from mesitylene by the method of Hinkel, Ayling, and Morgan (*J.*, 1932, 2797); it had b. p. 116—118°/12 mm., n_D^{21} 1·5531 and solidified at 0°. The semicarbazone crystallised from methanol as plates, m. p. 186°. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate-chloroform as red plates, m. p. 250—251° (Found: C, 58·5; H, 5·1; N, 17·0. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9; N, 17·1%).

2-*Methylacetophenone*.—This was prepared from 2-methyl-3 : 6-dihydroacetophenone by dehydrogenation with chromic acid instead of chloranil (cf. Braude, Jones, Sondheimer, and Toogood, *J.*, 1949, 607). A solution of chromium trioxide (1·7 g.) and sulphuric acid (2·7 g.) in water (6 ml.) was added dropwise to a cooled solution of the dihydro-compound (3 g.) in acetone (10 ml.). The mixture was kept at room temperature overnight and then diluted with water. The product was isolated with ether and the fraction of b. p. 92—93°/16 mm. was converted to the semicarbazone (1·8 g.) m. p. 198—200°, raised to 204° by crystallisation from ethanol (Auwers, *Annalen*, 1915, **408**, 242, gives m. p. 203°). The semicarbazone was refluxed with light petroleum (50 ml.; b. p. 60—80°) and 2N-sulphuric acid (50 ml.) under nitrogen, with mechanical stirring. After 45 min., the clear petroleum layer was separated, dried, and evaporated, giving 2-methylacetophenone (1·1 g.), b. p. 93°/17 mm., n_D^{23} 1·5235.

2 : 6-*Dimethylacetophenone* [with R. L. ERSKINE].—A solution of methyl-lithium in ether

(10 ml.) was added to 2 : 6-dimethylbenzoic acid (0·36 g.; prepared as above) in ether (8 ml.). After 1 hr., the mixture was poured into water. The ethereal layer was separated, dried (Na_2SO_4), and distilled, giving 2 : 6-*dimethylacetophenone* (0·22 g.), b. p. 114—116°/21 mm., n_D^{20} 1·5222 (Found: C, 80·75; H, 8·15. $C_{10}H_{12}O$ requires C, 81·05; H, 8·15%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in orange needles, m. p. 154—155° (Found: N, 17·6. $C_{16}H_{16}O_4N_4$ requires N, 17·1%) [Pearson and Greer (*J. Amer. Chem. Soc.*, 1955, **77**, 1294) give m. p. 159°]. Schwartzman and Corson (*ibid.*, 1954, **76**, 784) give b. p. 111°/23 mm., n_D^{20} 1·5162, $\varepsilon < 2000$ at 2500 Å, for the ketone and state that it fails to give a 2 : 4-dinitrophenylhydrazone. In our hands, a sample of their product, kindly provided by Dr. Schwartzman, on treatment with Brady's reagent at room temperature, readily furnished a 25% yield of derivative which, after chromatography on alumina in benzene and crystallisation from benzene had m. p. 223°, $\lambda_{max.}$ 4070 ($E_{1\,cm.}^{1\%}$ 900) and 4450 Å ($E_{1\,cm.}^{1\%}$ 1150) in $CHCl_3$ (Found: C, 52·5; H, 4·5; N, 17·8%; *M*, in camphor, 510).

Most of the experimental work was carried out in 1947—49 while one of us (F. S.) was in receipt of a Senior D.S.I.R. Award which is gratefully acknowledged.

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