

## POSSIBLE EFFECT OF HYPERCONJUGATION ON SOLVOLYSIS RATES OF BENZHYDRYL CHLORIDES\* AND SPECTRA OF RELATED COMPOUNDS†

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**Abstract** - The near ultraviolet absorption spectra of a series of benzcycloalkenes have been determined. A minimum in the absorption band near  $270\text{ m}\mu$  has been observed for benzcycloheptene. It appears significant that this same inflexion occurs in the solvolysis rates for the related benzhydryl chlorides. The data indicate that hyperconjugation plays an important role, and an explanation is offered in terms of the Franck-Condon principle.

THE absorption band near  $260\text{ m}\mu$  in benzene is caused by the transition of a  $\pi$  electron. For reasons of symmetry, this transition is a so called forbidden transition, and leads to an absorption band of low intensity.<sup>1</sup>

Methyl substitution in benzene causes a shift towards longer wavelengths and brings about an intensification of this band. Molecular orbital calculations have led to the conclusion that the bathochromic shift of this O, O band results from hyperconjugation.<sup>2</sup> The intensification of the transition by alkyl groups is associated with a transition moment produced by a migration of charge into the benzenoid ring.<sup>3, 4</sup> According to Mulliken,<sup>5</sup> "this migration of unsaturation-electron charge implies hyperconjugation."

Furthermore, a decrease in wavelength, as well as in intensity, for the O,O band in alkylbenzenes follows the order: toluene, ethylbenzene, isopropylbenzene and *tert.*-butylbenzene. This order can be explained by a decrease in the contribution by hyperconjugation,<sup>6</sup> although an alternative explanation has been proposed.<sup>7</sup>

For reasons which are not completely understood at present, the effect of alkyl groups on the absorption in the near ultraviolet region by aromatic compounds is not consistent. For example, in contrast to the "hyperconjugative order" mentioned above for the aromatic hydrocarbons, the intensities of the absorption bands for *para*-alkyl-substituted nitrobenzenes and aromatic ketones follow an "inductive order" (i.e., *tert.*-butylbenzene > isopropylbenzene > ethylbenzene > toluene).<sup>8</sup>

\* From the Ph.D. Thesis of W. R. Moore, University of Minnesota (June 1954).

† From the Ph.D. Thesis of Erich Marcus, University of Minnesota (June 1956).

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<sup>1</sup> H. Spomer, G. Nordheim, A. L. Sklar and E. Teller, *J. Chem. Phys.* **7**, 207 (1939).

<sup>2</sup> V. A. Crawford, *J. Chem. Soc.* 2061 (1953).

<sup>3</sup> A. L. Sklar, *J. Chem. Phys.* **10**, 135 (1940).

<sup>4</sup> A. L. Sklar, *Rev. Mod. Phys.* **14**, 232 (1942).

<sup>5</sup> R. S. Mulliken, *Rev. Mod. Phys.* **14**, 265 (1942).

<sup>6</sup> F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Rev.* **41**, 273 (1947).

<sup>7</sup> V. J. Hammond, W. C. Price, J. P. Teeagan and A. D. Walsh, *Disc. Faraday Soc.* **9**, 53 (1950).

<sup>8</sup> W. M. Schubert, J. Robins and J. L. Haun, *J. Amer. Chem. Soc.* **79**, 910 (1957), and earlier papers.

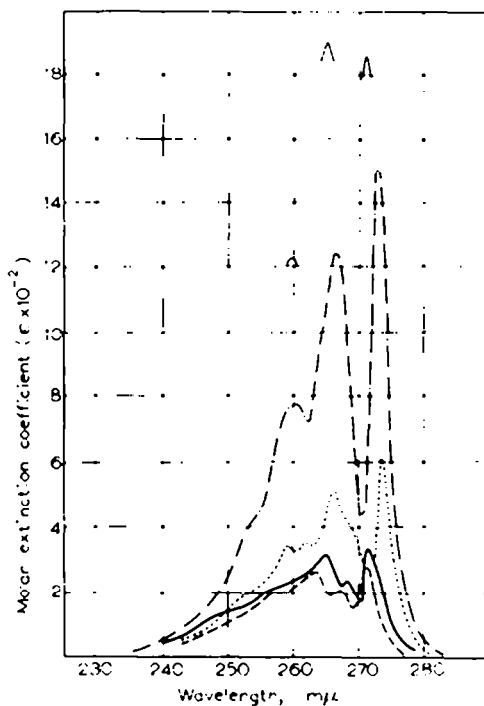
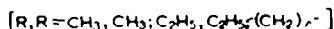
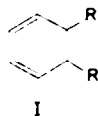


FIG. 1. Benzcyclobutene (peaks only) (---); benzcyclopentene (- · - · -); benzcyclohexene (· · · · ·); benzcyclooctene (—); benzcycloheptene (— — —).

Of particular interest in the present study is the effect of cyclization on the absorption spectra of 1,2-dialkylbenzenes. Remart-Lucas and Hoch<sup>9</sup> compared the spectra of *o*-xylene and indan in the region near 270  $m\mu$  and concluded that the absorption bands for these two compounds—aside from mere fine structure—were essentially the same. This conclusion, referred to in later review articles,<sup>10, 11</sup> is not in agreement with our data, which show that the O,O band in indan (benzcyclopentene) is some sevenfold more intense than that for *o*-xylene.

Table 1 summarizes pertinent absorption data for a series of 1,2-dialkylbenzenes (I) and Fig. 1 provides more detailed information on several of these.



It is apparent from Table 1 that all of the 1,2-benzocycloalkenes which we have studied absorb more strongly near 270  $m\mu$  (i.e., the O,O transition) than does *o*-xylene. This same generalization holds also for the more highly substituted derivatives

<sup>9</sup> P. Remart-Lucas and M. J. Hoch, *Bull. Soc. Chim. Fr.* (5) 2, 327 (1935).

<sup>10</sup> R. N. Jones, *Chem. Rev.* 32, 28 (1943).

<sup>11</sup> G. Kortüm and G. Dreesen, *Chem. Ber.* 84, 182 (1951).

TABLE 1. ULTRAVIOLET ABSORPTION OF 1,2-DIALKYLBENZENES (I)

Compound	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max}$ (95% ethanol)	$\epsilon_{\max}$ (isooctane)
$n = 2$	271	(1860) <sup>12</sup>	—
$n = 3$	273	1450	1500
$n = 4$	274	627	620
$n = 5$	271	292	277
$n = 6$	272	344	325
<i>o</i> -Xylene	271	—	(204), (212) <sup>13</sup>
<i>o</i> -Diethylbenzene	271	—	(200), (208) <sup>14</sup>

having substituents in the 1,2,4,5, positions.<sup>15</sup> In addition, it will be observed that the intensity of absorption drops rapidly from benzcyclobutene to benzcycloheptene, and then a small but definite rise occurs for benzcyclooctene.

This inflexion, in the absence of other data, might not have been regarded as significant. We are intrigued, however, by the fact that this same inflexion has been found in the first-order solvolysis rates for the substituted benzhydryl chlorides (II), as shown in Table 2.\*

TABLE 2. RELATIVE RATES OF SOLVOLYSIS (90% ACETONE) OF CHLORODIBENZCYCLOALKENYLMETHANES (II)

$n$	Relative rates		Activation energy (kcal/mole)
	0	25°	
3	2.94	2.42	16.4
4	1.62	1.56	17.3
5	1.00	1.00	17.6
6	1.25	1.19	17.3

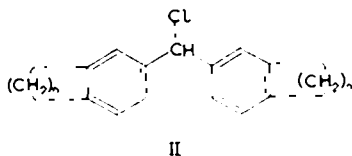
\* It is intended that the preparation of and kinetic data for these compounds will be given in detail in a subsequent article.

<sup>12</sup> M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.* **78**, 500 (1956).

<sup>13</sup> Amer. Petroleum Inst. Res. Project 44, Serial Nos. 43 and 55 (1945).

<sup>14</sup> Amer. Petroleum Inst. Res. Project 44, Serial Nos. 77 and 186 (1945, 1947).

<sup>15</sup> Erich Marcus, W. M. Lauer and R. T. Arnold, *J. Amer. Chem. Soc.* **80**, 3742, (1958).



It is possible, of course, that the inflexion which has been found to be a common feature of the above-mentioned spectral and rate studies may be fortuitous. We prefer, however, to believe otherwise. An examination of earlier published data,<sup>6, 16, 17, 18</sup>

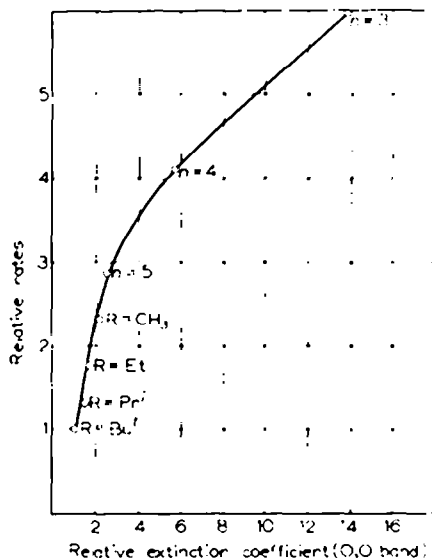
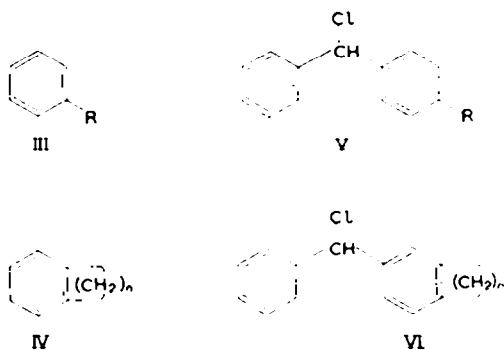


FIG. 2. Relative rates of hydrolysis of compounds (V) and (VI) (80° acetone, 0') vs. relative molar extinction coefficients of related hydrocarbons (III) and (IV).

combined with some results from the present study, as shown in Fig. 2, suggests a relationship between the intensities of absorption (at peak nearest 270  $m\mu$ ) of the hydrocarbons represented by (III) and (IV) and the solvolysis rates for the related benzhydryl chlorides (V) and (VI).



<sup>16</sup> E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.* 949 (1940).

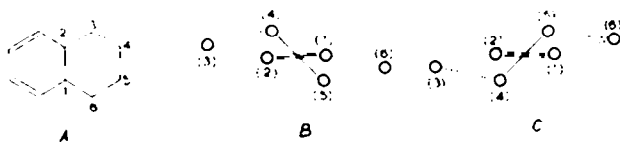
<sup>17</sup> R. T. Arnold and W. L. Truett, *J. Amer. Chem. Soc.* 73, 5508 (1951).

<sup>18</sup> G. Baddeley and M. Gordon, *J. Chem. Soc.* 2190 (1952).

Although we recognize the importance of steric effects which may increase solvation energies<sup>8, 19</sup> and lead to a diminution in the solvolysis rates of benzhydryl chlorides, it should be pointed out that the variations found in Tables 1 and 2 can be rationalized in terms of steric factors which could determine, in large part, the extent to which hyperconjugation comes into play in these molecules.

### DISCUSSION

Let us now consider in more detail the geometry of tetrahydronaphthalene and indan, because it is in these cases where the most significant change in extinction coefficients occurs. The ground state of tetrahydronaphthalene is represented by (A) and the partial (and exaggerated) formulac—which represent conformations—by (B) and (C), as follows:



Tetrahydronaphthalene, because of its "zig-zag" structure, has stable conformations (B and C) such that  $C_4$  and  $C_5$  are alternately above and below the plane of the ring and  $C_3$  and  $C_6$  are here assumed to be slightly above or below the plane of the ring, depending on the positions of  $C_4$  and  $C_5$ .\*

The excited state—in which hyperconjugation plays a more prominent role—is indicated below by formula (D) and a crude representation of the extreme conformations by (E) and (F) as seen from a point in the plane of the benzenoid ring:



In the excited state, it is expected that a stronger bond will exist at  $C_1-C_6$  and  $C_2-C_3$ . For purposes of simplification, let us consider the  $C_{A_1}-C_{A_1}$  out-of-plane vibrations. Out-of-plane vibrations of the  $C_2-C_3$  bond in the excited state should have a smaller amplitude than the same vibrations in the ground state. If a plot is made of the potential energy of this model against the angle ( $\theta$ ) of out-of-plane vibration, the picture shown in Fig. 3 will be obtained.

According to the Franck-Condon principle, the angle  $\theta$  cannot be changed during an electronic transition. Therefore, the transition is forbidden for those molecules where  $\theta > \theta_1$ . The fraction of molecules that can make the transition is a factor in determining the transition probability and, therefore, the absorption band intensity.

In benzcyclobutene (I;  $n = 2$ ), the conformations in the ground and excited states must be very similar. According to our view, this would account for the high absorption observed for this molecule, and leads us to predict a high rate of solvolysis for the corresponding benzhydryl chloride when it finally becomes available.

\* We thank Dr. Bryce L. Crawford for stimulating and useful discussions on these points.

<sup>19</sup> C. C. Price and W. J. Belanger, *J. Amer. Chem. Soc.* **76**, 2682 (1954).

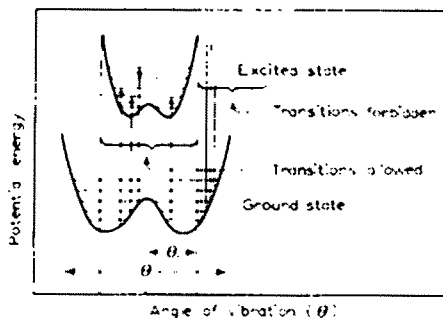


FIG. 3. Potential-energy diagram (qualitative) for tetrahydronaphthalene.

Although indan ( $I; n = 3$ ) is not a completely planar molecule, we believe that the difference in the out-of-plane vibrations in the ground and excited states is much smaller than that in tetrahydronaphthalene, and that its potential-energy diagram may be qualitatively represented by Fig. 4.

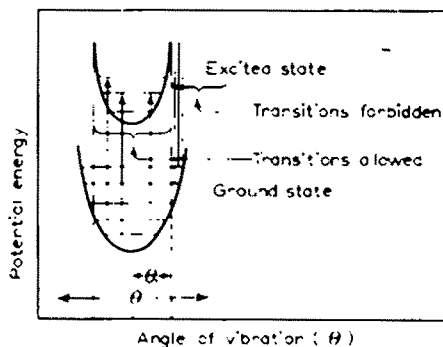
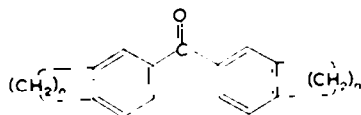


FIG. 4. Potential-energy diagram (qualitative) for indan.

Molecular models of the compounds reported on here do indicate an extreme out-of-plane position for the  $\alpha$ -methylene carbon atoms in benzcycloheptene ( $I; n = 5$ ), and an application of the above argument offers a reasonable explanation for the minima which we are reporting for spectral and rate data in this series.

Finally, a careful examination of Courtauld or Fischer-Hirshfelder-Taylor models for benzcyclooctene ( $I; n = 6$ ) indicates that the molecule can assume many conformations, all of which involve a considerable degree of intramolecular crowding. Although it includes a great deal of speculation, we have concluded that the difference in the amplitude of the  $C_{A_7}-C_{A_1}$  out-of-plane vibrations in benzcyclooctene in the ground and excited states should be smaller than that for benzcycloheptene, and thus permit a greater probability of transition from ground to activated state. This, then, accounts for the interesting inflexion referred to earlier in this paper.

Schubert and co-workers<sup>8</sup> have pointed out, quite convincingly, the difficulty of explaining the spectra of *p*-alkylacetophenones on the basis of hyperconjugation. In the course of the present study, we examined the ultraviolet spectra for the benzophenone derivatives (VII), and the pertinent data are included in Table 3.



VII

(n=3,4,5,6)

TABLE 3. ULTRAVIOLET ABSORPTION OF DIBENZCycloALKENYL KETONES (VII)

n	<i>iso</i> Octane (solvent)		95% Ethanol (solvent)	
	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max} \times 10^{-2}$	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max} \times 10^{-2}$
3	262	203	270	181
4	263	221	271	199
5	263	227	271	206
6	264	236	271	211

With respect to ring size vs. intensity of absorption, it will be seen (i) that the order followed in Table 1 is almost the reverse of that found in Table 3 and (ii) no inflexion occurs at  $n = 5$  in Table 3. We are unable, at present, to explain these differences.