[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

The Steric Requirements for Three-Ring Carbonyl Hyperconjugation[1]

BY NORMAN H. CROMWELL AND GLENN V HUDSON

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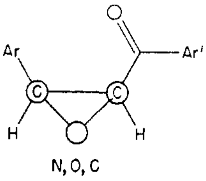
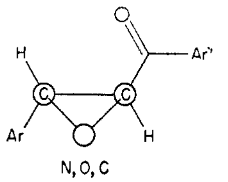
The ultraviolet and infrared absorption spectra of perinaphthenone-7, perinaphthanone-7 and 8,9-epoxyperinaphthanone-7 have been measured. These results along with those previously reported[4] for 8,9-[*n*-cyclohexyl]-iminoperinaphthanone-7 indicate that the carbonyl groups in the perinaphthanone-7 compounds have similar polarities. It therefore seems that three-ring carbonyl hyperconjugation of three-rings fused to a six-membered ring containing an adjacent endocyclic carbonyl group makes only a slight contribution to the excited state and none at all to the ground state of such molecules. The steric requirements for such orbital overlapping seems to be that the π-orbitals of the attached unsaturated groups must be able to orient themselves so that their axes are parallel with the plane of the three-ring, and thus symmetrically arranged with respect to the ($2s - 2p\sigma$) hybridized orbitals of the three-ring carbon atoms.

In a previous publication we described by the use of molecular orbital as well as valence bond qualitative language and suitable diagrams, the electron interactions possible between three-rings and formally unsaturated groupings (carbonyl and aryl) attached to these rings.[2] It was there pointed out that in the *trans* forms of aryl aroyl ethylenimines, ethylene oxides and cyclopropanes the π-orbitals of the formally unsaturated atoms can be arranged to give the maximum overlapping with the *bent bond* hybridized orbitals of the two three-ring carbon atoms. This orbital orientation provides for more extensive polycentric molecular orbitals than are possible with the sterically inhibited *cis* geometrical isomers. In these latter structures it is seen from models that appreciable overlapping between the attached carbon atom π-orbitals and the *bent bonds* of the three-rings is not to be expected. It seems necessary that there be orbital overlap with two carbons of the three-ring and attached unsaturated groups to obtain appreciable electron interaction.[2]



cis



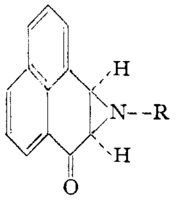
trans

This hyperconjugation makes a considerable contribution to both the *ground* and *excited* states of the *trans* aryl aroyl ethylenimines. It has been predicted,[2] reasoning from relative polarities, that in the case of the analogous ethylene oxides and cyclopropanes only the *excited* states will prove to be significantly affected by such electronic interactions. Consequently only the ultraviolet spectra comparisons of *cis* and *trans* isomers should show differences in these latter cases.

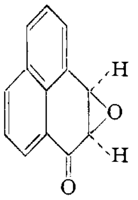
These theoretical ideas have been supported by the spectra studies which have been made to date.[2,3]

In the present paper we wish to call further attention to the demanding steric requirements which bear upon the opportunity for this type of hyperconjugation.

If Fig. 2 of the previous article[2] is a meaningful representation of the orbital orientation responsible for this interaction between the electrons of the three-ring and the carbonyl group then it is implied that the π-orbital bearing carbon atoms must have some freedom of rotation about the sigma bonds attaching them to the two three-ring carbon atoms. That is, they must be able to orient themselves in such a manner as to have *the axes of their π-orbitals parallel with the plane of the three-ring and symmetrically arranged with respect to the bent bonds.* This is a case where it is not a totally sufficient requirement for electron interaction in the conjugated system to simply have the component atoms all in the same plane. If the two π-orbital bearing carbon atoms and the two three-ring carbons to which they are attached are a part of the same six-membered ring the above italicized conditions cannot be met. Consequently, we would not expect either 8,9-(N-cyclohexyl)-iminoperinaphthanone-7[4] (I) or 8,9-epoxyperinaphthanone-7[5] (II) to show much three-ring carbonyl hyperconjugation. In both of these structures the axes of the π-orbitals of the carbon atoms attached to the three-ring carbon atoms cannot be arranged parallel to the plane of the three-ring. Such a geometrical arrangement would be expected to disallow an appreciable overlapping with the *bent bond* molecular orbitals of the three-rings in these molecules.



I



II

It was therefore to be expected that both the ultraviolet and infrared spectra studies of these perinaphthanone-7 three-ring derivatives would indicate their carbonyl groups to be of about the same polarity as that of the CO group present in the parent saturated ketone, perinaphthanone-7. In fact the entire ultraviolet spectra and the carbonyl stretching vibration frequencies in the infrared should be similar for all three compounds.

Absorption Spectra.—The ultraviolet absorption spectra curves for carefully purified samples of perinaphthenone-7, perinaphthanone-7 and 8,9-epoxyperinaphthanone-7 in isoöctane are shown in Fig. 1. The curve for 8,9-(N-cyclohexyl)-iminoperinaph-

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[1] Presented at the 122nd Meeting of the American Chemical Society, Atlantic City N. J., Sept. 17, 1952.

[2] N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952).

[3] N. H. Cromwell, *et al.*, THIS JOURNAL, **73** 1044 5929 (1951).

[4] N. H. Cromwell, D. B. Capps and S. E. Palmer, *ibid.*, **73**, 1226 (1951).

[5] L. F. Fieser and L. W Newton, *ibid.*, **64**, 919 (1942).

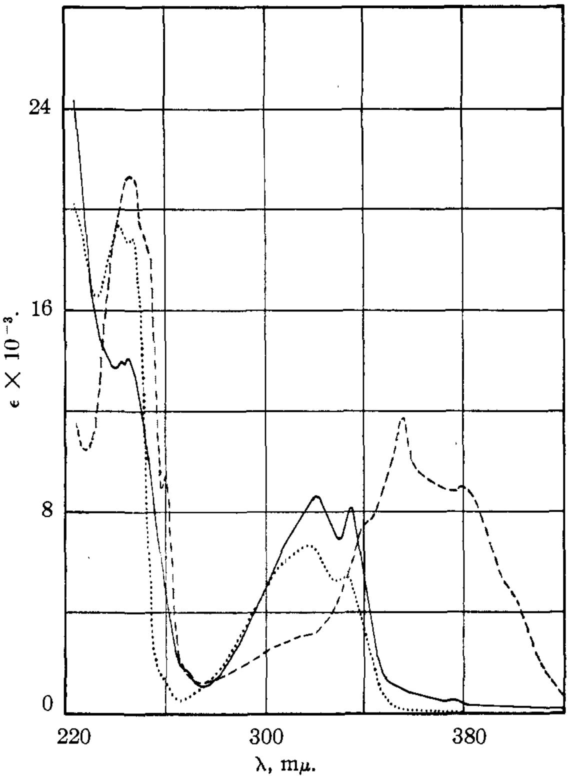


Fig. 1.—Ultraviolet absorption spectra of: perinaphthenone-7, ---; perinaphthanone-7, . . . ; and 8,9-epoxyperinaphthanone-7, —, in 2,2,4-trimethylpentane solution.

thanone-7 (previously misnamed as a perinaphthenone) was included in an earlier report.[4] The spectra for the perinaphthanones are all quite similar to each other and very different from that of the perinaphthenone-7. It is seen that the additional conjugated unsaturation in the latter substance intensifies the two longer wave length absorption bands and shifts them considerably toward the red end of the spectrum.

The infrared spectra for perinaphthenone-7, perinaphthanone-7 and 8,9-epoxyperinaphthanone-7 are given in Fig. 2, and that for 8,9-(N-cyclohexyl)-iminoperinaphthanone-7 has been reported previously.[4] The characteristic absorption bands to be associated with the carbonyl bond stretching vibrations in the solid compounds were found from 1670 to 1685 cm.$^{-1}$ for the perinaphthanone-7 compounds and at 1637 cm.$^{-1}$ for the perinaphthenone-7.

It is thus established that three-ring carbonyl hyperconjugation makes no contribution to the ground states and only a slight one to the excited states in ethylenimines and epoxides of types (I) and (II). The polarities and single bond characters of the carbonyl groups in perinaphthanone-7 and its three-ring derivatives are not very different.

A comparison of the ultraviolet absorption spectrum in Fig. 1 and the infrared absorption spectrum from 1650 to 1550 cm.$^{-1}$ in Fig. 2 for perinaphthenone-7 with the results previously[4] reported for 8-amino- and 9-aminoperinaphthenone-7 compounds show some striking similarities. The presence of the amino group in the 9-position actually has an hypsochromic effect on the ultraviolet longer wave length absorption maxima, although the intensities of these are somewhat increased. The polarities of the carbonyl groups in these substituted and unsubstituted unsaturated ketones are similar and there seems to be little carbonyl–amino group interaction, especially in the ground state. In the open chain conjugated unsaturated systems the introduction of an amino group into the position beta to the carbonyl group has a profound effect upon both the ultraviolet spectrum and the infrared band associated with the carbonyl stretching vibration. For example β-morpholinobenzalacetophenone has its characteristic carbonyl band at a frequency[6] of 1628 cm.$^{-1}$ and its ultraviolet long wave length absorption maximum at λ, 328 mμ.[7] For chalcone (benzalacetophenone) the corresponding values are 1655 cm.$^{-1}$ and 299 mμ, respectively. These facts taken together might be explained by considering the importance of canonical forms (C) as providing for maximum electron mobility (orbital overlap) in these structures. Form (C), for geometrical reasons, could make no contribution to the endocyclic β-amino-α,β-unsaturated ketone structures. Further evidence for this explanation is being sought.

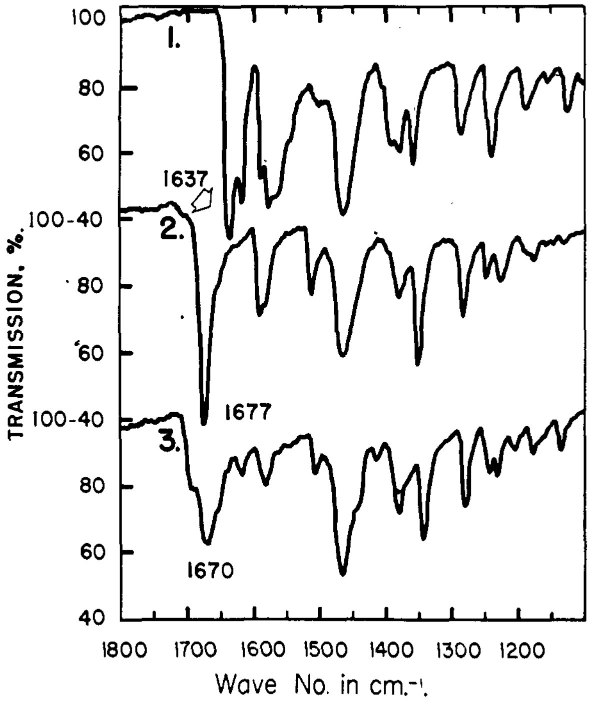
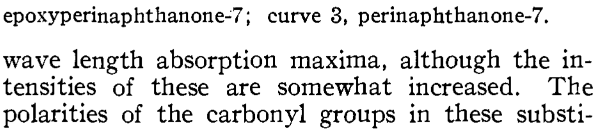


Fig. 2.—Infrared absorption spectra traced from the original curves covering the range of 600 to 4000 cm.$^{-1}$ using a NaCl prism: curve 1, perinaphthenone-7; curve 2, 8,9-epoxyperinaphthanone-7; curve 3, perinaphthanone-7.



It is possibly worth pointing out that the elec-

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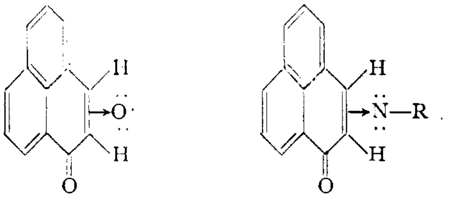
(6) N. H. Cromwell, *et al.* THIS JOURNAL, **71**, 3337 (1949).

(7) N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, **14**, 411 (1949).

tron distribution implied by so-called π-bond structures for either the epoxides[8a] or the ethylenimines[8b] as have been offered by others would not suggest the low level of hyperconjugation in these molecules and thus such pictures are not very useful in describing the properties of these compounds.



π-bond structures

On the other hand our findings may be offered as strong verification for the usefulness of the previously[2,9] suggested molecular orbital pictures of such structures. It is now seen that the requirement of proper orientation of the π-orbital bearing carbons attached to the three-ring carbons must be rather critically met if appreciable three-ring hyperconjugation is to take place. Our studies of these steric factors are being continued.

Acknowledgment.—A portion of the work described here was done under a grant to one of us from the National Science Foundation, Research Grant NSF-G57.

Experimental

Preparation and Purification of Materials.—The perinaphthenone-7 for these experiments was prepared by the method of Fieser and Hershberg[10] and recrystallized several times from methanol and then from benzene and petroleum ether mixtures; m.p. 153.5–154.5°.

8,9-Epoxyperinaphthanone-7 was prepared by the method described by Fieser and Newton[6] and purified by chromatographing on activated alumina to free the crude product from considerable amounts of perinaphthenone-7. The material was deposited on the column from a solvent mixture of four parts of 60–70° boiling petroleum ether and three parts of benzene. The column was developed with a mixture of two parts of benzene to one part of petroleum ether and then the purple and brown colored bands eluted with pure benzene. The lowest band was purple in color and eluted as a pale yellow solution. This first eluate contained all of the desired pure 8,9-epoxyperinaphthanone-7. It formed pale yellow needles on recrystallization from benzene and petroleum ether, m.p. 123–124°. The brown colored band eluted as a bright yellow solution and was shown to consist mainly of perinaphthenone-7.

Perinaphthanone-7 was prepared by the method of Fieser and Gates,[11] m.p. 84°.

Absorption Spectra.—The *ultraviolet-visible* absorption spectra were determined at about 25° using 2,2,4-trimethylpentane (Spectro Grade, Eastman Kodak Co.) 10^{-4} molar solutions and a Beckman model DU photoelectric quartz spectrophotometer employing 10-mm. silica cells; see Fig. 1. The *infrared* absorption spectra were determined at about 25° using Nujol mulls of the compounds and a Perkin-Elmer recording infrared spectrophotometer Model 21 by Dr. H. S. Gutowsky of the University of Illinois; see Fig. 2.

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[8] (a) A. D. Walsh, *Nature*, **159**, 165, 712 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949); (b) E. Boyland, *Biochem. Soc. Symposia*, No. 2, 61 (1948), Great Britain.

[9] C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, [7] **40**, 1 (1949).

[10] L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **60**, 1658 (1938).

[11] L. F. Fieser and M. D. Gates, *ibid.*, **62**, 2335 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Benzidine Rearrangement. Kinetics and Temperature Coefficients of the Rearrangements of Hydrazobenzene and Certain Substituted Hydrazobenzenes[1]

BY LOUIS J. CROCE AND JOSEPH D. GETTLER

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The rates of rearrangement of hydrazobenzene and a number of substituted hydrazobenzenes have been determined. A positive linear salt effect has been established, dielectric constant effects have been studied and energies and entropies of activation have been obtained. The effect of substituents has been shown to influence the energies and entropies of activation in a linear fashion. The rate has been shown to be second order with respect to the hydrogen ion concentration.

Introduction

Relatively few kinetic studies of the benzidine rearrangement have been made up to the present time. Van Loon[2] studied the rate of formation of benzidine in several mixed solvents and in the presence of various acids. His results indicated that the rearrangement is first order with respect to the hydrazobenzene concentration and second order with respect to the hydrogen ion concentration. Bulman and Bloom[3] obtained the rate of rearrangement of two *p,p'*-disubstituted hydrazoanilines by measuring the rate of their disappearance using a potentiometric method. Dewar,[4] using a chemical method involving the reduction of a dye, obtained the rates, the temperature coefficients and thermodynamic quantities of hydrazobenzene and three symmetrically substituted hydrazobenzenes. Recently, Hammond and Shine[5] indicated that Dewar's interpretations of his results do not consider the effect of acid concentration in the rate expression. Hammond and Shine using the analytical method of Dewar firmly established the second-order dependency of the rate of rearrangement on the oxonium ion concentration and they observed a positive salt effect on the rate. These authors propose the reaction sequence

$$C_6H_5NHNHC_6H_5 + H^+ \rightleftarrows C_6H_5N^+H_2NHC_6H_5 \tag{A}$$

$$C_6H_5N^+H_2NHC_6H_5 + H^+ \rightleftarrows C_6H_5N^+H_2N^+H_2C_6H_5 \tag{B}$$

$$C_6H_5N^+H_2N^+H_2C_6H_5 \longrightarrow H_2NC_6H_4C_6H_4NH_2 + 2H^+ \tag{C}$$

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[1] This paper is based in part on a thesis submitted by Louis J. Croce to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Evans Research and Development Corporation, New York, N. Y.

[2] J. P. Van Loon, *Rec. trav. chim.*, **23**, 62 (1904).

[3] E. Bulman and J. H. Bloom, *J. Chem. Soc.*, **125**, 1719 (1924).

[4] M. J. S. Dewar, *ibid.*, 777 (1946).

[5] G. Hammond and H. J. Shine, THIS JOURNAL, **72**, 220 (1950).