TABLE V

COMPARISON OF SOLVENT VISCOSITIES AND RELATIVE RATE CONSTANTS AT WAVE LENGTH OF MAXIMUM ABSORPTION

Solvent	η (centipoise) at 20°	$k/\epsilon_c \times 10^{-6}$ at λ_{max} (cm. sec.$^{-1}$) (from Fig. 1)	$\eta k/\epsilon_c \times 10^{-4}$ (poise cm. sec.$^{-1}$)
Benzene	0.652	3.2	2.09
Toluene	.590	3.6	2.12
o-Xylene	.810	2.5	2.02
p-Xylene	.648	3.8	2.46
Mesitylene	.702[a]	1.8	1.26

[a] Measured in this Laboratory with an Ostwald viscometer calibrated with benzene.

carbon tetrachloride and hexachlorobutadiene-1,3.

Although Mulliken's charge-transfer theory predicts that the extinction coefficient should increase with decreasing donor ionization potential or increasing stability of the complex,[5] just the opposite behavior is observed in most cases.[23] A solution to this discrepancy has been proposed in terms of a contact charge-transfer spectrum (whereby the donor and acceptor species are close to each other but do not complex), either as a result of interaction between the charge-transfer state and the ground states of the donor and acceptor[24] or between the charge-transfer state and the donor-excited states.[25] In either case, if there is a mixture of complex and contact spectra, the contribution of the contact charge-transfer band would be expected to become less important with increasing complex stability. Therefore, one might expect the values of the extinction coefficient to pass through a minimum with increasing complex stability, as observed in this work (Fig. 1) where it is assumed (although not known) that the I atom complexes are more stable than comparable I_2 complexes and that increasing donor methylation increases the stability of the complex. Also, if the I atom–aromatic complex is highly symmetric with the atom centered over the benzene ring, there will be no contribution by the donor-excited states and the behavior should be as predicted by Mulliken for a complex spectrum. (As pointed out by Murrell,[25] this may be the case with complexes involving chloranil as the acceptor, for which the bands are also considerably less intense than those for comparable I_2 systems.)

Acknowledgments.—Valuable aid was obtained from Dr. J. W. Hollingsworth, Mr. W. G. McClintock and Mr. S. Tsao of the Computer Laboratory, Rensselaer Polytechnic Institute, in the computer work reported. We gratefully acknowledge support in part by National Science Foundation Grants NSF G-4181 and G-9988.

---

[23] S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958).

[24] L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957).

[25] J. N. Murrell, *ibid.*, **81**, 5037 (1959).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY, NEW YORK, NEW YORK]

The Determination of Double-bond Character in Cyclic Systems. V. Proton Chemical Shifts in Chelated Derivatives of Benzene, Naphthalene and Phenanthrene[1,2]

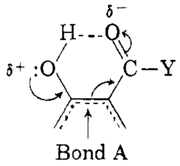
BY A. L. PORTE,[3] H. S. GUTOWSKY AND I. MOYER HUNSBERGER

RECEIVED FEBRUARY 15, 1960

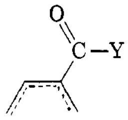
The OH proton chemical shifts are measured for phenol, β-naphthol, 9-phenanthrol, and for chelated *o*-substituted derivatives of each containing an aldehyde, methyl ketone and methyl ester group. The large amounts ($\Delta\delta$) by which the shifts to lower applied fields are greater in the chelated derivatives than in the parent phenols are measures of the strengths of the intramolecular hydrogen bonds and are proportional to the bond multiplicity of the ring bonds between the carbon atoms holding the chelated substituents. The $\Delta\delta$ values are also proportional to $\Delta\nu$(C=O) values determined earlier from infrared spectra of the same compounds. Mechanisms responsible for the proton chemical shifts are discussed.

Introduction

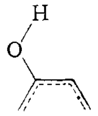
Previous papers[4,5] in this series have demonstrated that conjugated chelation of *ortho* carbonyl and hydroxyl groups in benzene, naphthalene and phenanthrene, lowers the C=O stretching frequency of the chelated compound (I) below that of the parent carbonyl compound (II) by an amount $\Delta\nu$(C=O) which is proportional to the per cent. double-bond character (%DBC) of the ring bond (Bond A) between the carbon atoms holding the chelated substituents. Characteristic $\Delta\nu$(C=O) values were obtained for the benzene bond, the 1,2- and 2,3-bonds of naphthalene, and the 9,10-bond of phenanthrene by examining the infrared spectra of the appropriate hydroxyaldehydes, hydroxyketones and hydroxyesters. For a given bond, the $\Delta\nu$(C=O) values consistently increased in proceeding from the hydroxyaldehyde to the hydroxyketone to the hydroxyester, but



I



II



III

Y = —H, —CH_3, and —OCH_3

---

[1] Paper IV: I. M. Hunsberger, H. S. Gutowsky, W. Powell, L. Morin and V. Bandurco, THIS JOURNAL, **80**, 3294 (1958).

[2] Acknowledgment is made to the donors of The Petroleum Research Fund, administered by The American Chemical Society, for partial support of this research. Support was also received from the National Science Foundation (Grant G-7640 to I.M.H.) and from the Office of Naval Research.

[3] Noyes Chemical Laboratory, University of Illinois, Urbana, Ilinois.

[4] I. M. Hunsberger, THIS JOURNAL, **72**, 5626 (1950).

[5] I. M. Hunsberger, R. Ketcham and H. S. Gutowsky, *ibid.*, **74**, 839 (1952).

the difference between the $\Delta\nu$(C=O) values obtained from the hydroxyketone and the hydroxyesters was small. In accord with theoretical expectations, straight lines having different slopes were obtained when each set of $\Delta\nu$(C=O) values was plotted against the %DBC of the aromatic bond in question.[5]

Very recently Heinert and Martell[6] determined $\Delta\nu$(C=O) values of 45 and 38 cm.$^{-1}$, respectively, for the 2,3- and the 3,4-bonds of pyridine by comparing the infrared spectra of 3-hydroxy-2- and 4-pyridinecarboxaldehydes with those of 2- and 4-pyridinecarboxaldehyde. These $\Delta\nu$(C=O) values combined with those we obtained from the naphthalene[4] and phenanthrene[5] hydroxyaldehydes gave an excellent straight line graph when plotted against the appropriate molecular orbital (m.o.) bond orders.

In present-day theoretical discussions of the structure of aromatic hydrocarbons, m.o. bond orders tend to be used to the virtual exclusion of the more naive concept of %DBC but it is necessary to emphasize that equally good linearity is obtained regardless of whether our $\Delta\nu$(C=O) values for benzene, naphthalene and phenanthrene are plotted against %DBC, m.o. bond order, or valence bond (v.b.) bond order. This result is indeed required in that, for the three hydrocarbons named above, each of these three methods of describing bond order is linearly related to the others. The only disadvantage of using v.b. bond orders is that no reliable value appears to have been calculated for the 9,10-bond of phenanthrene.

In our original work in the benzene and naphthalene series[4] we had hoped to use $\Delta\nu$(OH), *i.e.* $\nu(\mathrm{OH})_{\mathrm{I}} - \nu(\mathrm{OH})_{\mathrm{III}}$, as a measure of the strength of the hydrogen bond in I and hence of the %DBC in bond A. This expectation was thwarted by the fact that, in most of the compounds examined, the OH absorption in I was shifted so far to longer wave length that it merged with the CH absorption. Also the shifted OH band was broad, thus making its accurate location difficult. Only in the relatively weakly bonded 3,2-disubstituted naphthalenes was it possible to assign $\Delta\nu$(OH) values. It is interesting to note that the $\Delta\nu$(OH) value increased slightly in going from the hydroxyester to the hydroxyaldehyde, whereas the $\Delta\nu$(OH) for the hydroxyketone was very much larger.

Changes in the electron distribution in the neighborhood of a hydrogen atom occur when it takes part in hydrogen bonding and so proton magnetic resonance techniques can detect, and have been used to detect and to study, hydrogen bonding.[7] These changes should be particularly large in the strong intramolecular hydrogen bonds with which we are concerned and so it seemed to us that magnetic resonance techniques would afford an excellent method for measuring the relative strengths of these bonds.

The present paper summarizes some such studies we have carried out on many of the same chelated *o*-substituted derivatives of phenol, β-naphthol and 9-phenanthrol which had been studied earlier by infrared. The proton chemical shift, $\Delta\delta$, in going from III to I will be shown to be analogous to $\Delta\nu$(OH) in the infrared method. The use of $\Delta\nu$(OH) was severely limited for the reasons given above. However, $\Delta\delta$ appears to be generally applicable to the study of bond multiplicity in aromatic ring systems.

Experimental

All compounds used in this work were the same samples as those described previously[4,5] except that those which had deteriorated on standing were purified before use. Thanks are due to Messrs. John L. Ferrari, Claude V. Greco, Donald J. Howard and John J. Maitner for the purification work.

The proton magnetic resonance spectra were all recorded with a Varian Associates V-4300B high-resolution spectrometer[8] working at a fixed frequency of 40 Mc. Except where otherwise stated, carefully purified samples of each substance were studied in dilute solution in carbon tetrachloride, and in the case of the chelated derivatives the concentration ranges studied varied from 100 to 20 g./l.

All spectra were recorded at 25°, using cyclohexane as an internal reference standard, and the chemical shifts were all referred to the cyclohexane peak. The shifts are given in parts per million, *i.e.*

$$\delta = \text{chemical shift} = \left(\frac{H(\text{cyclohexane}) - H(\text{observed})}{H(\text{cyclohexane})}\right)10^6$$

The standard deviations in the measured chemical shifts are all of the order of 0.025 part per million. The effect, $\Delta\delta$, of the conjugated chelation upon the shift of the OH group proton is defined as

$$\Delta\delta = \delta(\text{chelated derivative}) - \delta(\text{parent phenol})$$

Only one absorption peak was observed for the $-$OH proton in the substituted compounds, and no change in the spectrum could be detected when the solutions were diluted with carbon tetrachloride. It therefore follows that in carbon tetrachloride solution at room temperature, the derivatives exist effectively in the chelated form.

Results and Discussion

Phenol and its Chelated *o*-Substituted Derivatives.—The OH proton chemical shifts observed for phenol (see Fig. 1) in carbon tetrachloride solution increased linearly with concentration up to a maximum of 5.55 p.p.m. at a concentration of 135 g. per l., and the shift did not change at higher concentrations. The lowest concentration studied was 24 g. per l., and extrapolation afforded 3.93 p.p.m. as the magnitude of the chemical shift at infinite dilution. This value does not agree either with that given by Saunders and Hyne[9] or with the value of 2.80 p.p.m. quoted by Pimentel, Shoolery and Huggins.[10] Later on in this paper we will reconcile our value with that quoted by the latter authors. The chemical shifts observed in some chelated *o*-substituted derivatives of phenol are given in Table I.

Chemical shifts in general result from electronic interactions within the sample and from interactions

---

[6] D. Heinert and A. E. Martell, THIS JOURNAL, **81**, 3933 (1959).

[7] See, for example, J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," Ch. 15, McGraw-Hill Book Co., Inc., New York, N. Y., 1959, and references therein. See also P. J. Frank and H. S. Gutowsky, *Arch. Sci.* (*Geneva*) **11**, 215 (1958).

[8] A detailed description of the apparatus has been deposited as Document number 6086 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be obtained by citing the Document number and by remitting $27.50 for photoprints, or $7.75 for 35-mm. microfilm, in advance by check or money order payable to Chief; Photoduplication Service, Library of Congress.

[9] M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958).

[10] C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

TABLE I

The OH proton chemical shifts δ and Δδ, in p.p.m., and the Δν (C=O) values, in cm.$^{-1}$, of phenol, β-naphthol, 9-phenanthrol, and some of their chelated *o*-substituted derivatives, in infinitely dilute solution in carbon tetrachloride. The chemical shifts, δ, are downfield from and relative to cyclohexane.

	δ	Δδ	Δν (C=O)
Phenol	2.80	..	..
Methyl salicylate	9.14	6.34	47
Salicylaldehyde	9.55	6.75	38
o-Hydroxyacetophenone	10.63	7.83	45
β-Naphthol	3.2	..	..
Methyl 2-hydroxy-1-naphthoate	10.72	7.52	68
2-Hydroxy-1-naphthaldehyde	11.48	8.28	51
2-Hydroxy-1-acetonaphthone	11.85	8.65	60
Methyl 3-hydroxy-2-naphthoate	8.74	5.54	32
3-Hydroxy-2-naphthaldehyde	8.74	5.54	27
3-Hydroxy-2-acetonaphthone	9.85	6.65	28
9-Phenanthrol	3.5	..	..
10-Hydroxy-9-phenanthrenecarboxaldehyde	12.95	9.45	61
Methyl 10-hydroxy-9-phenanthryl ketone	13.25	9.75	75

between the externally applied magnetic field and the electrons in the sample.[7] When an external magnetic field is imposed on a molecule, it induces a change in the magnetic moment associated with each electron and this change, which depends on the electronic wave function, is directed in such a way that it opposes the applied field. Each induced electronic magnetic dipole then gives rise to a secondary magnetic field at a nucleus, in the direction of the externally applied field, given by $H(\text{secondary}) = -(3\cos^2\theta - 1)\langle\Delta\mu\rangle/r^3$ where $\langle\Delta u\rangle$ is the average value of the induced moment, r is the length of the vector joining $\langle\Delta u\rangle$ and the nucleus, and θ is the angle between this vector and the applied magnetic field. If the nucleus lies on a line at right angles to the center of the induced dipole, then the secondary field is $\langle\Delta u\rangle/r^3$ in the same direction as the applied magnetic field. If, however, the nucleus lies on the axis of the induced dipole, then the secondary field is $-2\langle\Delta u\rangle/r^3$ and it opposes the applied field.

All the electrons in a molecule, and in neighboring molecules, exert secondary fields at each nucleus and, therefore, the applied external magnetic field at which each nucleus absorbs radiation of fixed frequency is a function of the electron distribution in the "free" molecule, of the molecular geometry, and of the distances of approach of neighboring molecules. In the chelated derivatives of phenol the –OH proton resonance at "infinite dilution" is shifted to lower applied magnetic fields than that of phenol itself. The contributions to this difference can be regarded as being derived from two main types of effect: (i) "direct" magnetic effects and (ii) electrostatic effects.

The "direct" magnetic effects arise through the substitution of the group $\text{Y—}\overset{|}{\text{C}}\text{=O}$ for the *ortho* hydrogen atom of phenol, since in an applied magnetic field the resultant dipole induced in this group differs from that induced in the replaced hydrogen atom. In general, since more electrons are involved, the magnetic dipole induced in the $\text{Y—}\overset{|}{\text{C}}\text{=O}$ group should be expected to be greater than that associated with a single hydrogen atom. However, Pascal's work on classical diamagnetism shows that the second order paramagnetic term[11] in a carbonyl group is appreciable[12] and this term will tend to cancel out the diamagnetic effects of the substitution, except for the contribution due to the diamagnetic moment induced in one of the lone pair σ-orbitals of the oxygen atom. This is the σ-orbital involved in the chelate hydrogen bond and the moment induced in it exerts an appreciable secondary field at the –OH proton because of its very close proximity to it.

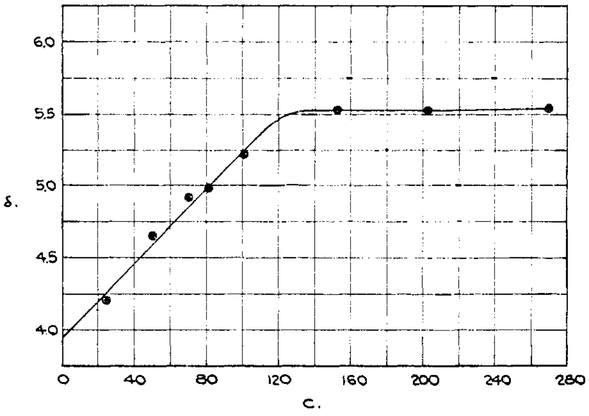


Fig. 1.—The hydroxyl proton chemical shift (δ), in p.p.m. downfield from cyclohexane, in phenol as a function of the concentration (*c*) of phenol in carbon tetrachloride, in g./l. of solution.

Indirect magnetic effects due to changes in the electron density on the hydroxyl and carbonyl oxygen atoms and to the changes in electron density in the aromatic ring tend to cancel each other and their net effect is relatively small.

The electrostatic contribution to the shift arises, in large part, from the very close distance of approach of the lone pair σ-orbitals of the carbonyl oxygen atom to the –OH hydrogen during the formation of the hydrogen bond. These strongly repel the electrons which are in the neighborhood of the hydrogen nucleus and therefore reduce the diamagnetic shielding of that nucleus by its own electrons and increase the paramagnetic "unshielding."[7] A second electrostatic contribution arises from the mesomeric shift of the π-electrons away from the –OH, through the aromatic ring, to the C=O group. The resultant charges on the oxygen atoms distort, by induction, the electron density on the –OH hydrogen atom and therefore also decrease the diamagnetic shielding of this hydrogen nucleus by its own electrons.

The observed OH proton chemical shifts are very large, of the order of 400 cycles down-field from cyclohexane at an applied frequency of 40 Mc., and the absorption peaks occur at positions

---

(11) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932.

(12) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, page 52.

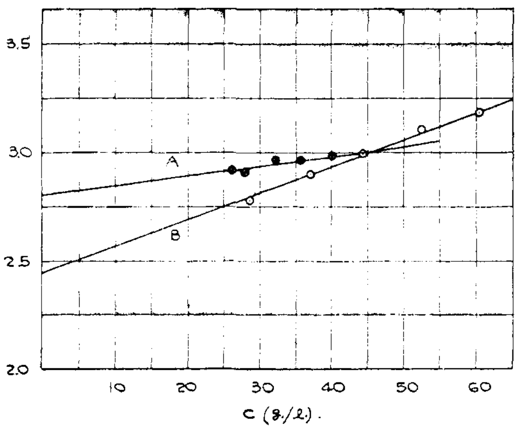


Fig. 2.—The hydroxyl proton chemical shifts (δ), in p.p.m. downfield from cyclohexane, in β-naphthol (A) and phenol (B) as a function of concentration in benzene solution (C), in g./l. of solution.

normally associated with strongly acidic protons. However, it does not necessarily follow that these chelated compounds are strong acids. Also, it should be noted that the large shifts in concentrated solutions of phenol result from the strong *inter*-molecular hydrogen bonding which produces phenol polymers.[9,10] The interactions responsible for the proton shifts in the latter are no doubt very similar to those occurring within the chelated *o*-substituted derivatives.

The relative values of the chemical shifts in the chelated derivatives themselves reflect the difference in the tendency of the group Y (in I) to alter the electron density on the carbonyl oxygen atom. The tendency to increase electron density on this atom is well known to increase as Y varies from $-OCH_3$ to $-H$ to $-CH_3$ and results in movement of the proton peak to lower applied fields in the sequence observed.

β-Naphthol and its Chelated *o*-Substituted Derivatives.—Since β-naphthol is almost insoluble in non-polar solvents, it was necessary to estimate the position of the resonance absorption peak characteristic of the OH proton of an isolated β-naphthol molecule in carbon tetrachloride solution by the following indirect method. The chemical shift of the OH proton in solutions of β-naphthol in benzene was measured as a function of concentration (Fig. 2) and then extrapolated to infinite dilution. The value thus obtained was 2.80 p.p.m. This shift is not the same as that in carbon tetrachloride solution because an OH group can form weak hydrogen bonds with an aromatic nucleus in which the OH bond is directed along the normal to the center of the aromatic ring, *i.e.*, there is a tendency for the benzene molecules to pack round the OH groups so that the OH bond points along this normal rather than to the side of the ring. The currents induced in the π-electron system in the benzene when an external field is applied then exert a secondary magnetic field at the OH proton and this secondary field opposes the applied field. The result is an upfield shift of the proton resonance for the OH group in the β-naphthol-benzene "complex," with respect to the resonance for an isolated β-naphthol molecule.

In order to obtain an estimate of the magnitude of this "complexing effect" in terms of chemical shift, the proton resonance spectrum of phenol was re-examined in benzene solution (Fig. 2). The phenolic proton absorption peak at infinite dilution in benzene is 2.45 p.p.m., a value which is displaced by 1.48 p.p.m. toward higher applied magnetic field as compared with the results obtained in carbon tetrachloride. The magnitude of this shift can be accounted for when it is remembered that the six π-electrons circulating, under the influence of an applied magnetic field, in the plane of a benzene ring lying at right angles to the magnetic field vector are equivalent[13] to a magnetic dipole of moment $\mu = 3e^2Ha^2/2mc^2$ where a is the radius of the benzene ring, and e and m are the electronic charge and mass, respectively. This dipole is situated at the center of the ring and directed along the normal to the ring. If the angle between the plane of the benzene ring and the applied field vector is averaged over all orientations, the average value for the induced dipole becomes $\langle\mu\rangle = e^2Ha^2/2mc^2$. In the "complex," this magnetic dipole exerts a secondary magnetic field at the OH proton of H (secondary) = $-2\langle\mu\rangle/r^3$ and causes a chemical shift of $-e^2a^2/mc^2r^3 = -55.15/r^3$ p.p.m. when r is expressed in Å.

The hydrogen bond between an OH group and an aromatic nucleus is a weak one and the H—benzene distance would be expected to be of the order of 2.5 Å. if the complex existed in the solid state. In solution, however, the distance must be much greater than this, and it is not constant since the weak bonds continually are being broken and re-formed again. An average value for r of about 3 to 3.5 Å. will be reasonable. If r is taken to be 3.3 Å. then the above reasoning gives a shift of 1.53 p.p.m., in good agreement with the observed value of 1.48 p.p.m.

It therefore seems reasonable to assume that the model proposed to describe the packing of the benzene molecules in the neighborhood of the OH group is essentially correct. Furthermore, there seems to be no reason why the benzene molecules should not pack round the OH group of β-naphthol in the same way. If this is so, a solvent shift of the same magnitude can be anticipated for β-naphthol. Certainly, if a solvent shift of 1.5 p.p.m. is allowed for β-naphthol, then we shall not be too far from the true value. Hence, the extrapolation of the OH proton absorption peak to infinite dilution of β-naphthol in carbon tetrachloride solution is taken to be (2.80 + 1.5) or 4.3 p.p.m. Thus the β-naphthol OH proton absorbs at a slightly lower applied field than the corresponding peak in phenol. This small difference is accounted for by: (i) a contribution of 0.15 p.p.m. from the induced currents in the additional aromatic ring and (ii) a very small difference in the electron density in the neighborhood of the hydrogen nucleus. β-Naphthol is a slightly stronger acid than phenol.

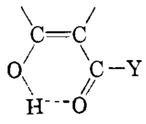
The extrapolated values of 3.93 and 4.3 p.p.m. for the OH proton absorption peaks of phenol and

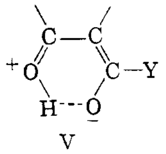
---

[13] J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

β-naphthol are not the characteristic shifts of the monomers of these substances in infinitely dilute carbon tetrachloride solution. Saunders and Hyne[9] and Huggins, Pimentel and Shoolery,[10] find that the plot of chemical shift *vs.* concentration for phenol, curves sharply at points involving OH concentrations lower than that which our instrument was able to detect. The latter authors quote a value of 2.80 p.p.m. for phenol and so, for consistency, we displace our shifts at infinite dilution by 1.1 p.p.m. to obtain characteristic shifts of 2.8 and 3.2 p.p.m. for the monomers of phenol and β-naphthol in carbon tetrachloride solution. We believe that the error involved in the β-naphthol monomer shift using this procedure will not be more than about 0.15 p.p.m.

The chemical shifts of the OH protons in some chelated *o*-substituted derivatives of β-naphthol are given in Table I. As was the case with the corresponding derivatives of phenol, the sequence of chemical shifts is hydroxyester < hydroxyaldehyde < hydroxyketone. In each series of compounds studied it is seen that the chemical shift increases on going from the 3,2-naphthalene derivative to the benzene derivative to the 2,1-naphthalene derivative. The amount (Δδ) by which the shift, to lower applied field, in the chelated derivative differs from that of its parent phenol also increases in this same sequence, and these increases reflect the differences in the mesomeric effects in the three groups of derivatives. As is well known, the mesomeric effect defines the relative importance of the canonical forms IV and V in the chelated conjugated molecule. Thus, an increase in the hydroxyl proton shift results from an increasing contribution from form V, which in turn increases as the double-bond character of the C=C bond in IV increases. Hence, the proton chemical shift increases as the double-bond character of this C=C bond increases. Furthermore, since the contribution from V parallels the strength of the hydrogen bond, the Δδ values should be a direct measure of the relative strength of this bond in the compounds examined.


IV


V

Within each of the series, ester, aldehyde and ketone, the Δδ values only measure the relative mesomeric contributions provided there are no steric strains to alter the geometry from the idealized unstrained structures visualized above. Only in the case of the aldehyde derivatives do we feel certain that steric effects are of negligible importance.

9-Phenanthrol and its Chelated *o*-Substituted Derivatives.—Since 9-phenanthrol is unstable in air, it was purified and stored under nitrogen. Furthermore, all solutions were prepared in a nitrogen atmosphere. Since this compound is insoluble in carbon tetrachloride, the chemical shift of its OH proton was estimated in a manner similar to that described for β-naphthol. At infinite dilution in benzene, this shift was found to be 3.11 p.p.m. If a solvent shift of 1.5 p.p.m. and an extrapolation shift of −1.1 p.p.m. are again allowed, the shift for 9-phenanthrol at infinite dilution in carbon tetrachloride is 3.5 p.p.m. (Table I), a value considerably larger than that for β-naphthol, as expected on the basis of our arguments. The trends in chemical shifts in phenol, β-naphthol and 9-phenanthrol follow those already observed for the ν(OH) values[5] (Table II).

TABLE II

OH STRETCHING FREQUENCIES AND HYDROXYL PROTON CHEMICAL SHIFTS, AT INFINITE DILUTION, IN PHENOL, β-NAPHTHOL AND 9-PHENANTHROL

	ν(OH) (cm.$^{-1}$)[a]	Chem. shift (p.p.m.)[b]
Phenol	3628	2.8
β-Naphthol	3618	3.2
9-Phenanthrol	3605	3.5

[a] Values taken from Paper II, I. M. Hunsberger, R. Ketcham and H. S. Gutowsky, THIS JOURNAL, 74, 4839 (1952). [b] We are indebted to Professor L. W. Reeves of the University of British Columbia for reviewing our results and pointing out a systematic error which we have corrected in our values listed here for the "isolation shifts." In addition he informed us that he has measured a shift of 3.49 p.p.m. for β-naphthol at infinite dilution, which indicates that our indirect method of obtaining the OH proton shifts for β-naphthol and 9-phenanthrol is substantially correct.

All the chemical shifts of the chelated 9,10-disubstituted phenanthrenes (Table I) are more toward lower applied fields than those of the corresponding 2,1-disubstituted naphthalenes. This indicates a larger amount of double bond character for the 9,10-bond of phenanthrene.

Bond Multiplicity as Measured by Δδ from Proton Magnetic Resonance Data.—When the Δδ values for the hydroxyaldehydes and for the hydroxyketones are plotted against some measure of the bond multiplicities in benzene, the 1,2- and 2,3-bonds of naphthalene, and the 9,10-bond of phenanthrene, respectively, straight line graphs of differing slopes are obtained (Fig. 3). We have defined the bond multiplicities in Fig. 3 in terms of mobile bond orders[14] because no reliable v.b. calculation appears to have been made for phenanthrene. It follows that the Δδ values in the hydroxyaldehyde and hydroxyketone series are proportional to the multiplicity of that C to C bond (in the parent hydrocarbon) spanned by the chelated system.

The equations which relate mobile bond order with Δδ are, for the hydroxyaldehydes, $\Delta\delta = 23.47$ (mobile bond order) $-$ 8.75, and for the hydroxyketones, $\Delta\delta = 17.92$ (mobile bond order) $-$ 4.19. In the case of the esters a linear relationship of this sort cannot be given, presumably because of steric effects which we will discuss in a forthcoming paper.

The above equations predict that in the imaginary, chelated, hydroxyaldehyde and hydroxyketone in which the C—C mobile bond order is zero, VI, the OH proton resonance should be upfield from that of the corresponding imaginary alcohol with zero mobile bond order by amounts $(\Delta\delta)_0$ of −8.75 and −4.19 p.p.m., respectively, and according to our earlier arguments these figures should represent

---

[14] C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants, Vol. II," Mathematical Institute, Oxford, and references therein.

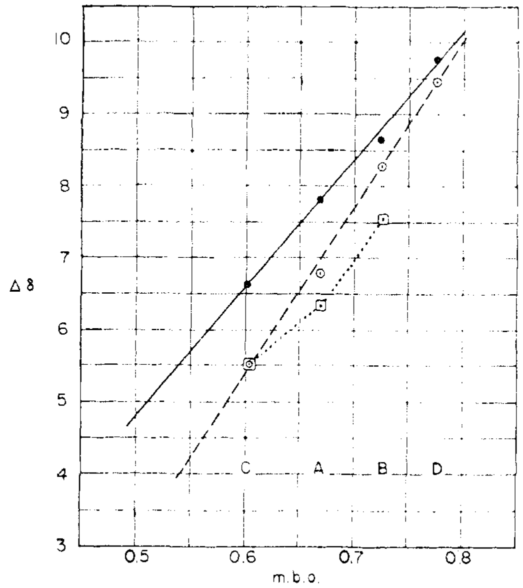


Fig. 3.—Δδ values, in p.p.m., of chelated aldehydes (---------), chelated ketones (———) and chelated esters (......) as functions of mobile bond order (m.b.o.) of the C=C bond spanned by the chelated system. A larger Δδ value corresponds to a larger downfield shift and stronger hydrogen bonding. The compounds included are 1,2-disubstituted benzenes (A), 1,2-disubstituted naphthalenes (B), 2,3-disubstituted naphthalenes (C) and 9,10-disubstituted phenanthrenes (D).

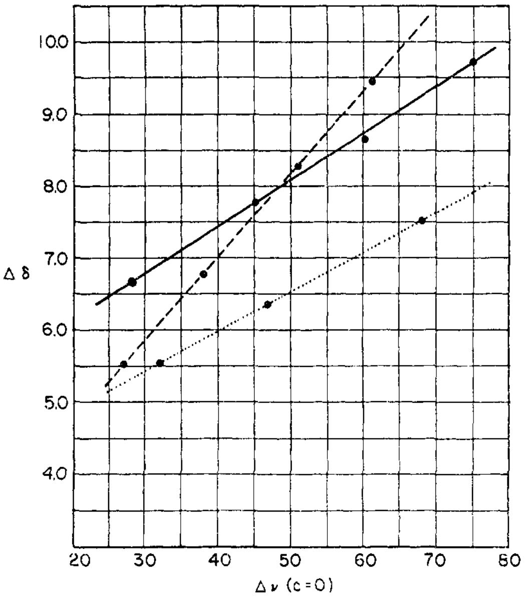
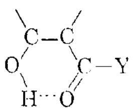
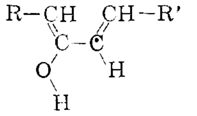


Fig. 4.—Δδ values, in p.p.m., of chelated aldehydes (---------), chelated ketones (———) and chelated esters (......) as functions of the corresponding Δν(C=O) values. A larger Δδ value corresponds to a larger downfield shift and stronger hydrogen bonding. The compounds included are listed in Table I.

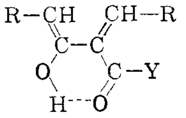
the Δδ values when no mesomeric effect is possible. They should represent those contributions to the



VI



VII



VIII

shifts which arise from the oxygen σ electrons involved in the hydrogen bond and from the ability of Y to release electrons to the carboxyl group. Both of these contributions should cause the OH proton resonance to move downfield relative to the parent alcohol and so the $(\Delta\delta)_0$ values obtained from the above equations are opposite in direction to the shifts predicted on the basis of our earlier arguments.

This inconsistency appears to imply that our earlier arguments are incorrect. This is not so, however, because we do not know whether our linear relationships are valid over all ranges of mobile bond orders, an uncertainty which would partly be cleared if our studies could be extended to include non-aromatic compounds such as VII and VIII. Moreover, even if the linear relationships are valid for the whole range of bond orders, a further difficulty arises in interpreting the physical meaning of the quantities $(\Delta\delta)_0$. These quantities are functions of the description of the double bond character of the bond C=C in I since if the observed shifts are plotted against valence-bond bond orders, different straight line graphs are obtained. This applies to Δν(C=O) as well. For example, if Δν(C=O) is plotted against mobile bond order instead of %DBC, the resulting lines are straight, but they no longer go through the origin. And if Δδ is plotted against %DBC, one finds positive Δδ intercepts for zero %DBC. This might have been anticipated because the molecular orbital and valence bond descriptions are not equivalent nor are they directly proportional to each other, even though linearly related. Presumably if all canonical forms and all the interactions between these forms were allowed for in the valence bond description and if complete configuration interaction was allowed for in the molecular orbital description, then the two sets of straight lines would converge and the $(\Delta\delta)_0$ values for VI could be predicted with confidence. The differences in the $(\Delta\delta)_0$ values represent the differences in the inductive effects of substituents Y, in terms of chemical shift of the OH proton, only if absolute C=C bond orders are used, but it should be noted that although we are not able to give absolute magnitudes for these differences, the relative qualitative effects cannot be inverted by the description of the bond order. Δδ in the hydroxyketone series is always greater than Δδ in the hydroxyaldehyde series, as should be expected since the CH_3 group donates electrons to the carbonyl group.

In conclusion, it is apparent that the position of the proton magnetic resonance peak of the OH proton in chelated derivatives of phenols is extremely sensitive to the C=C bond order in the parent hydrocarbon. If the mobile bond order is known, the chemical shift in the chelated compound may be predicted from the above relationships. Conversely, if the shift is known, then the bond order, or any property which is related to this bond order, may be predicted. Thus the Δν(C=O) values[4,5] may be predicted by use of the graphs in Fig. 4. These results may afford a rapid analytical method of locating the positions of chelated groups in aromatic systems. Fig. 4 shows that the $\Delta\delta$ values are linearly related to the $\Delta\nu$(C═O) values to a striking degree. The deviations of the points from the straight lines in this figure are much smaller than either the deviations from linearity in Fig. 3 or the corresponding deviations in the plot of $\Delta\nu$(C═O) values.[5] This again indicates that, in addition to the C═C mobile bond orders, some other effects are concerned in exact descriptions of the factors which influence the $\Delta\delta$ values and that these effects also influence the $\Delta\nu$(C═O) values. We believe that these other factors are mainly steric in nature.

Work is in progress in these Laboratories designed to determine $\Delta\nu$(C═O) values and proton shifts for chelated derivatives of the simple 5-membered heterocyclic rings.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, RIVER CAMPUS STATION, ROCHESTER, NEW YORK]

The Photochemistry of 1,3-Butadiene and 1,3-Cyclohexadiene[1]

BY R. SRINIVASAN

RECEIVED MARCH 7, 1960

The photolysis of 1,3-butadiene at 4 mm. pressure and room temperature with an unfiltered medium pressure mercury arc (mainly 2000–2500 Å.) led to hydrogen, acetylene, ethylene, ethane, 1-butyne, 1,2-butadiene, dimer(s) and a polymer as the major products and numerous minor products. A consideration of the stoichiometry, the effects of added gases and of increasing pressure, suggests that three primary processes which may arise from an excited state of the butadiene molecule are important. These are (1) $C_4H_6^* \rightarrow CH_2{=}C{=}CH{-}CH_3^*$ (the "hot" 1,2-butadiene molecule may subsequently decompose to give $CH_3\cdot$ and $C_3H_3\cdot$ radicals unless it is stabilized by a deactivating collision); (2) $C_4H_6^* \rightarrow C_2H_2 + C_2H_4$; (3) a process which leads to the formation of hydrogen. This may be $C_4H_6^* \rightarrow C_4H_4 + H_2$, although the formation of C_4H_4 was not proven. Preliminary results on the photolysis of 1,3-cyclohexadiene suggest that three analogous primary processes which lead to 1,3,4-hexatriene, $2C_2H_2 + C_2H_4$, and benzene and hydrogen are important. A second isomer also was observed to be formed in poor yield.

Introduction

The mercury photosensitized decomposition of 1,3-butadiene has been the subject of several studies.[2–5] The present study of the photochemistry of butadiene[6] was started in an attempt to see whether this compound would isomerize photochemically to cyclobutene. It may be stated even at this point that such a reaction was not observed. However, it became apparent that many of the products of the photochemical decomposition were common to the mercury photosensitized decomposition.[3,5] The present study was undertaken to find the primary processes in the photochemistry of butadiene and also to clarify some of the secondary processes in the mercury sensitized decomposition. An exploratory study of the photochemistry of cyclohexadiene was attempted in order to compare this with butadiene.

Experimental

Butadiene of 99.4% purity was obtained from The Matheson Co., Inc. It was distilled from −78 to −159° and degassed at about −110° before use. Cyclohexadiene from Farchan Research Laboratories was dried and distilled once *in vacuo*. By vapor phase chromatography, it was found to be free from impurities.

A conventional high vacuum apparatus in which the reactants did not come in contact with stopcock grease was used. Since the photolysis of either diene led to the deposition of a polymer on the walls of the cell, reproducible results were obtainable only in clean cells. Hence two identical quartz cells of 5.0 cm. diameter an 4.4 cm. length were used alternately. At the end of each experiment, the used cell was detached from the line and replaced by a clean one. The alignment of the cell in the optical path was made reproducible by the use of a jig. The used cell was cleaned with a hot mixture of concentrated nitric and sulfuric acids followed by hot concentrated sulfuric acid alone and washed with distilled water.

The light source was a Hanovia type S-100 medium pressure mercury arc lamp, used without filters. This lamp does not give the mercury resonance radiation in detectable amounts.

From the products, two fractions were removed at −195 and −159°, respectively. These were analyzed mass spectrometrically on a Consolidated Engineering Co. type 21-620 instrument. The remaining products along with the unreacted butadiene were introduced into a Perkin–Elmer Vapor Fractometer type 154-B fitted with a 3-meter Perkin–Elmer column material "D." This column material gave a satisfactory resolution of 1,2-butadiene from butadiene but not the latter from 1-butyne, especially when butadiene was present in great excess. Hydrocarbon products of molecular weight 78 or more had such high retention times on this column that analysis for them was not practical. A 2-meter column of material "A" (Perkin–Elmer) had to be used if the higher boiling products were to be separated and analyzed. A complete analysis to include compounds as complex as 4-vinylcyclohexene (b.p. 129°) involved two identical experiments.

Qualitative analysis of the products was based on the cracking pattern in the mass spectrometer[7] and the retention time on the vapor phase chromatograph. Quantitative analyses for 1,2-butadiene and 1-butyne were based on the areas under the peaks in the chromatogram.

In some of the results reported here, when an initial pressure of butadiene of 4 mm. was used, the conversions ranged from 10 to 15%. At higher pressures of butadiene and in the presence of added gases, the conversions were less than 10%. While these conversions are high in terms of accepted photochemical practice, they were made necessary by the need to obtain reasonable amounts of products for analysis and to establish the amount of butadiene which had reacted. A further discussion of this will be reserved for a later section.

---

(1) The author wishes to thank the National Science Foundation for a grant to the Department of Chemistry, University of Rochester, in support of this work.

(2) G. Gee, *Trans. Faraday Soc.*, **34**, 712 (1938).

(3) H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **12**, 484 (1944).

(4) D. H. Volman, *ibid.*, **14**, 467 (1946).

(5) J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).

(6) The name butadiene or cyclohexadiene used without any prefixed numerals will hereafter refer to the 1,3-compounds.

(7) The author wishes to express his thanks to Dr. F. P. Lossing of the National Research Council of Canada for the mass spectrometric identification of a sample of 1,2-butadiene.