yielded 44 mg. of bicyclo[2.2.2]octanol-2, $[\alpha]^{25}_{D}$ + 2.52° (CHCl$_3$, c 4.4), which was shown by analytical v.p.c. to contain 3% of equatorial bicyclo[3.2.1]octanol-2 and 56 mg. of pure axial bicyclo[3.2.1]octanol-2, $[\alpha]^{25}_{D}$ +1.85° (CHCl$_3$, c 5.6).

Acknowledgment.—We are indebted to Professor J. A. Berson for many valuable and stimulating discussions.

Nuclear Magnetic Resonance Identification of Substitutional Isomers in Chelated Polycyclic Aromatic Systems[1]

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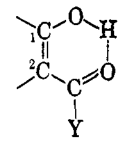
Some time ago we made a study of chemical shifts in chelated phenols which contain the structure I, where Y = -H, —CH$_3$, and -OCH$_3$, and from the results obtained[3] it seems likely that magnetic resonance methods may be useful in distinguishing between isomers of phenols with chelating substituents. The arguments which we will employ can easily be extended to other systems. The results exhibit two aspects by means of which the isomers may be distinguished on the basis of their high-resolution proton magnetic resonance spectra.

A. From the -OH Proton Chemical Shift.—In aromatic systems, the shift of a chelated -OH proton relative to the -OH peak in the corresponding parent phenol is quite large. We have found that this chemical shift is a linear function of the bond order of bond C-1=C-2, with the slope depending somewhat upon the substituent Y.[3] Therefore, the -OH proton shift in an unknown structure establishes whether or not the -OH group is *ortho* to substituent Y. If it is, the shift determines also the approximate bond order between the two carbons of the aromatic nucleus to which the -OH and -Y groups are attached. In turn, since approximate bond orders are known, and differ considerably for the various bonds in many aromatic systems, the bond order inferred from the -OH proton shift gives the location of the chelated structure in the molecule.

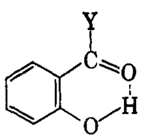
B. From the Chemical Shift of the Protons in Y.—A large part of the chemical shift of a proton, which is situated near an aromatic system, arises from the π-electronic ring currents induced in the aromatic system when the molecule is placed in a magnetic field.[4,5] It is this effect which leads to the other method of assigning the substituent position in polynuclear aromatic systems.

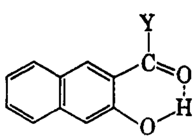

I

Method A is straightforward, direct, and requires little amplification.[3] Method B we will discuss in more detail. To a first approximation, the π-electron currents induced in each six-membered ring can be replaced by an elementary dipole situated at the center of the ring. Each dipole exerts a secondary magnetic field at Y, which is inversely proportional to the third power of the distance between the dipole and Y. This secondary field is in the same direction as the applied magnetic field, provided Y lies in the same plane as the aromatic system. If Y does not lie in this plane, then the effective field is reduced until, eventually, the applied field may be opposed by the secondary field. The maximum opposition to the applied field occurs when Y lies on the perpendicular drawn through the center of the dipole.

It is quite easy to show[4,5] that when Y does lie in the same plane as the aromatic system, then each secondary field causes a chemical shift of about 27.58/r^3 parts per million if r, the distance from the protons or other magnetic nuclei in Y to the π-electronic dipole, is expressed in angstrom units. Hence, if the dimensions of the molecule are known, the approximate relative chemical shifts of Y may be predicted for a series of similar compounds. These predicted shifts will be only approximately correct, because the π-electron systems are perturbed to different extents by interaction with the substituents, and this interaction, in its turn, modifies the diamagnetic circulations induced in the substituents. However, these effects are less important than the geometrical considerations outlined above, and they do not affect the qualitative arguments that are used.

The ring current shifts will be modified by solvent interactions, and so our arguments apply to solutions in which the solvent interactions are either negligible or very similar for the solutes in question.


II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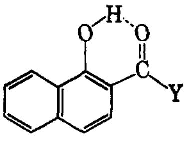
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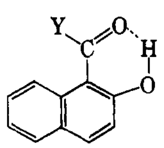
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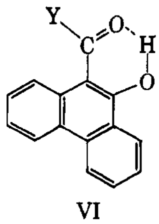
VI

With this qualification, one predicts that the downfield, ring-current shifts in compounds of types II to VI of the Y = H proton absorption peaks should be about 0.175 p.p.m. on going from I to III, somewhat less on going from II to IV, and about 0.55 p.p.m. on going from II and III to V and VI. These predictions

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[3] A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, *J. Am. Chem. Soc.*, **82**, 5057 (1960).

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

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co. Inc., New York, N. Y., 1959.

are in reasonable agreement with the observed shifts which in τ units are

	II	III	V	VI
Y = H	0.04	−0.09	−0.71	−0.57

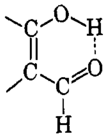
Here, negative values are downfield with respect to positive. These, and the other measurements given later, were made on dilute solutions in tetrachloride using cyclohexane as an internal reference.[3] The shifts were converted to the tetramethylsilane τ-scale by using a τ-value of 8.51 for cyclohexane.

In the case of the corresponding ketones, Y = CH_3, prediction of the ring current shifts is complicated by rotation about the C–CH_3 bond, but similar principles hold. The relative chemical shifts, however, will be smaller within this series than in the case of the aldehydes, because the protons of the –CH_3 group are further away from the elementary induced dipoles, and they do not lie in the same plane as the aromatic system. The observed shifts of the –CH_3 absorption peaks in τ units are

	II	III	IV	V	VI
Y = CH_3	7.35	7.21	7.23	7.14	7.19

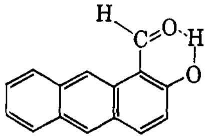
in qualitative agreement with the above arguments.

As an example of the use of these methods in structural determination, consider the position to be assigned to the –CYO groups in an hydroxyanthraldehyde (A) and in an hydroxyanthryl methyl ketone (B) which melt at 167 and 116°, respectively. In the case of the hydroxyanthraldehyde, chemical evidence[6,7] showed that the –OH group was at the 2-position, but it was not known whether the aldehyde group was at the 1- or the 3-position. The –OH proton line of A occurs at τ −3.64. This position is about 8.7_5 p.p.m. downfield from that expected[3] for the –OH position in either 1-hydroxy, or 2-hydroxyanthracene ($\tau \cong 5.1$) and is at the position expected for the chelated system VII

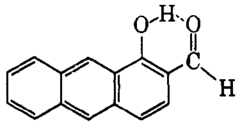


VIII

in which the mobile bond order of the C═C bond is 0.745.[3] Hence, it follows that the –OH and aldehyde groups are chelated and that the chelated system must span the 1–2 bond in the anthracene nucleus. It can not span the 2–3 position; *i.e.*, A is either VIII or IX on the basis of the –OH proton shift alone. Combining the –OH proton shift and chemical evidence, we find VIII to be the correct structure.



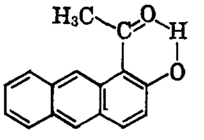
VIII



IX

The ring current effects enable us to confirm that VIII is the correct structure. The observed position of the –CHO absorption peak, at a τ-value of −0.87, is in the range predicted for structure VIII. For structure IX, the –CHO τ-value is predicted to be about −0.1, which differs so greatly from experiment that VIII must be the correct structure. This conclusion supports a structural determination based upon chemical arguments.[6,7]

In a similar way, the –OH and –CH_3 chemical shifts, with τ-values of −4.37 and 7.18 p.p.m., respectively, indicate[3] that B is X. In this case, the arguments based upon the –CH_3 group proton shift are not conclusive and the isomeric form with –OH and –$COCH_3$ groups interchanged was eliminated primarily by chemical evidence[6,7] as to the –OH position.



X

Experimental

The samples and experimental procedure, with one exception, were the same in these experiments as described in an earlier report.[3] The exception is the hydroxyanthraldehyde (A), the synthesis of which has been described elsewhere.[6,7] Furthermore, we are indebted to Professor I. Moyer Hunsberger for furnishing the samples and giving us some helpful comments on the manuscript.

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(6) J. L. Ferrari and I. M. Hunsberger, *J. Org. Chem.*, **25**, 485 (1960).

(7) J. L. Ferrari, Ph.D. thesis, Fordham University, 1962.

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trans-5-Cyclodecenone[1]

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Although studies of medium carbocycles (C_{8-11}) have yielded interesting information on interactions of functional groups with transannular double bonds,[2] the synthetic inaccessibility of the simplest systems has hindered a dissection of the nature of such interactions. One of the most promising methods of generating the exemplary 5-cyclononenyl and 5-cyclodecenyl systems is the fragmentation of appropriately substituted hydrindane and decalin precursors,[3] two further examples of which we report herewith for the stereospecific synthesis of *trans*-5-cyclodecenone (**4**).[2c]

Allylic alcohol **2**[4] prepared *via* photosensitized oxygenation of Δ^9-octalin,[4a] was converted to a mixture[5] of 1,10-decalindiols (**3a**) in 78% yield by the standard procedure using diborane.[6] The oily mixture of

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(1) This investigation was supported by a Frederick Gardner Cottrell grant from Research Corporation and by Public Health Service Research Grant GM 09759 from the Division of General Medical Sciences, U. S. Public Health Service.

(2)(a) See J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962), for a review and leading references. Later references include (b) A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962), and (c) H. L. Goering, *et al.*, *ibid.*, **83**, 3507, 3511 (1961).

(3) P. S. Wharton, *J. Org. Chem.*, **26**, 4781 (1961); E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 362 (1963).

(4) (a) G. O. Schenck and K. Schulte-Elte, *Ann.*, **618**, 185 (1958); (b) S. Dev, *J. Indian Chem. Soc.*, **34**, 121 (1957).

(5) Unpublished work has resulted in the separation of two crystalline *p*-nitrobenzoates of the oily diol mixture in yields of 50 and 20%.

(6) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **80**, 1552 (1958); **81**, 6428 (1959); and **84**, 183 (1962).