at 156° and a flow rate of 60 ml. per min. Retention times were for carbon tetrachloride 0.6 min., *n*-heptanoic acid 4.0, hexachloroethane 4.8, 1,1,1-trichloroheptane 6.2, dodecane 7.5, 1,1,1,3-tetrachloro-heptane 12.0 and hexyl heptanoate 25.7.

1,1,1,3-Tetrachloroheptane was determined on a 1-meter column with silicone oil 200 in series with a 1-meter Tide column, 182°, 1.1 atm., 45 ml. per min. Retention times were for cyclohexane 1.5 min., benzene 2.7, hexachloroethane 6.6, 1,1,1-trichloroheptane 7.5, dodecane 8.6, 1,1,1,3-tetrachloroheptane 15.0. Some samples showed a small peak at 6.2 min. in the former or at 7.5 min. in the latter system (1,1,1-trichloroheptane), but the amount was never more than 0.03 mole per mole of peroxide.

n-Hexyl *n*-heptanoate was determined on a 1-meter column of Dow-Corning silicone oil 550, temp. 245°, press. 0.7 atm., 45 ml. per min. Retention times were for carbon tetrachloride 0.4 min., hexachloroethane 1.0, dodecane 1.2, *n*-hexyl *n*-heptanonate 2.7.

In general it was not practical to make up standards in all solvent mixtures encountered. However, a large variety of standard solutions was employed, and the solvents did not usually show any appreciable effect on the peak area–concentration relationship.

In this work products were identified only on the basis of the retention time, but always in comparison with authentic samples of the compound (often on a series of columns) and by chemical reasonableness. From large scale runs in carbon tetrachloride the following compounds were isolated physically (moles per mole of peroxide are given in parentheses): CO_2 (1.62), 1-chlorohexane (1.0), dodecane (same), *n*-hexyl *n*-heptanoate (0.2), hexachloroethane (0.15), 1,1,1,3-tetrachloroheptane (0.1), and *n*-heptanoic acid (0.1).[27] Errors will tend to be those of overestimating the amount of a component by failure to recognize contamination by an unknown of similar retention time. Errors of selective underestimation are less likely.

[CONTRIBUTION NO. 2597 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

Chemical Shifts in $C_5H_5^-$, C_6H_6 and $C_7H_7^+$; Chemical Shifts and π-Electron Densities[1]

BY GIDEON FRAENKEL, ROBERT E. CARTER, ANDREW McLACHLAN[2] AND JOHN H. RICHARDS[3]

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The chemical shifts of several salts and derivatives of the cyclopentadienyl anion $C_5H_5^-$ and the tropylium cation $C_7H_7^+$ have been determined relatived to benzene as an internal standard in dimethyl sulfoxide and acetonitrile. The observed shifts are +1.85 and −1.9 p.p.m. for $C_5H_5^-$ and $C_7H_7^+$, respectively. These shifts are mainly accounted for by the electrostatic interaction between charge localized in the π-orbital of a carbon atom and the electrons in the C–H bond. The results, in conjunction with their theoretical interpretation, are used to determine "experimental" charge distributions in other aromatic systems.

Introduction

The π-electron density on the carbon atoms of conjugated molecules has an important effect on ring-proton chemical shifts[4]; however, in most organic compounds other factors such as ring currents[5-8] and the magnetic anisotropy of neighbors[9-11] are of great significance. In practice these three effects are not easily distinguished from one another.

In the isoelectronic series cyclopentadienyl anion $C_5H_5^-$, benzene C_6H_6 and tropylium cation $C_7H_7^+$,[12-14] each molecule has six π-electrons to contribute to the ring current, and the radii of the rings are so similar that the resulting screening[5] is, in every case, almost the same. Therefore, the relative hydrogen shifts in a *common solvent* should be almost entirely due to the different electron densities; moreover the π-electron densities in these species are known by their symmetry.

The total shifts were first determined by Leto, Cotton and Waugh[15] relative to an external standard in three different solvents. These values have now been measured in two common solvents, and the origin of the chemical shifts in these species and other aromatic compounds has been investigated theoretically. An electrostatic model has been derived that, in the main, accounts for our results and can be used to determine charge distributions in other aromatic molecules.

Experimental

Chemicals.—Acetonitrile, b.p. 82°, was distilled from phosphorus pentoxide. Dimethyl sulfoxide (Stephen Chemical Co., Chicago, Ill.) was dried by passage through a column of Linde molecular sieve powder. Tetrahydrofuran (Matheson) was treated with potassium hydroxide, refluxed, and distilled at 66° from lithium aluminum hydride and stored in an atmosphere of nitrogen in the refrigerator. Dicyclopentadiene (Enjay Co., New York) was cracked at 210° and the cyclopentadiene distilled, b.p. 42°, immediately before use. Ferrocene was kindly supplied by du Pont. Ruthenocene and osmocene were prepared by E. Alexander Hill, III.

Cyclopentadienylsodium.[16]—Equimolar quantities of cyclopentadiene and sodium sand were stirred in tetrahydrofuran under a nitrogen atmosphere at room temperature to produce an intensely purple solution of cyclopentadienylsodium.

Cyclopentadienyllithium.[17]—Cyclopentadiene was treated with an equimolar amount of phenyllithium in ether at 0° under an atmosphere of helium. The white precipitate was filtered and washed twice with ether and dried under helium.

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(1) Supported in part by the U. S. Public Health Service Grant No. 23332.

(2) Harkness Fellow of the Commonwealth Fund, 1959–1960.

(3) To whom inquiries concerning this work should be addressed.

(4) P. C. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956).

(5) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(6) J. A. Pople, *Mol. Phys.*, **1**, 175 (1958).

(7) J. A. Pople, *Proc. Roy. Soc.* (*London*), **A239**, 541 (1957).

(8) J. S. Waugh and R. W. Fessenden, THIS JOURNAL, **79**, 846 (1957).

(9) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(10) W. G. Schneider, H. J. Bernstein and J. A. Pople, *ibid.*, **28**, 601 (1958).

(11) A. A. Bothner-By and C. Naar-Colin, THIS JOURNAL, **80**, 1728 (1958).

(12) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(13) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(14) W. E. Doering and L. H. Knox, THIS JOURNAL, **76**, 3203 (1954).

(15) J. R. Leto, F. A. Cotton and J. S. Waugh, *Nature*, **180**, 978 (1957).

(16) D. Peters, *J. Chem. Soc.*, 1759 (1959).

(17) G. Jones and H. Gilman, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 353.

Magnesocene.[18]—Ethylmagnesium bromide was prepared by the reaction of equimolar amounts of ethyl bromide and magnesium in ether. The solvent was removed by distillation and simultaneously replaced by benzene until the temperature at the head of the distillation column reached 75°. An equimolar amount of cyclopentadiene was then added and the mixture stirred at 35–40° overnight. (The n.m.r. spectrum of the resulting benzene solution indicated that there was still present about one mole of bound ether per mole of magnesocene.) The brown solid that remained after removal of the solvent was sublimed at high vacuum, yielding magnesocene as white crystals.

Tropylium Fluoroborate.[19]—Cycloheptatriene (12 g., 0.13 mole) was added to phosphorus pentachloride (41 g., 0.197 mole) in 400 ml. of carbon tetrachloride. A white precipitate formed and the mixture was stirred for 24 hours. The solid was filtered, washed with carbon tetrachloride, and added in portions to 200 ml. of absolute ethanol at 0°. Fluoroboric acid (50% aq.) was added to the ethanolic solution until precipitation of the tropylium salt was complete. Recrystallization from ethyl acetate gave white crystals that decomposed above 210°.

N.m.r. Spectra.—All spectra were determined at 30° with the Varian 4300 B high resolution n.m.r. spectrometer equipped with superstabilizer, spinner and fixed frequency units for 60 Mc. The magnet cooling water was maintained at 27 ± 04°. The magnet yoke was insulated according to Varian specifications. Mounted on the center of each pole face were two 3-inch, 25-turn Helmholtz coils and one 25-turn circular coil built by Dr. R. P. Shafer for adjusting the x, y and z field gradients, respectively. Chemical shifts were measured by the method of audiosideband modulation using a Hewlett Packard frequency counter. All samples were sealed in 5-mm. o.d. Pyrex tubes under nitrogen and were stored in liquid nitrogen before use.

Results

The n.m.r. absorption of cyclopentadiene consists of two closely spaced multiplets at +0.84 and +4.4 p.p.m. relative to benzene as an internal solvent, as shown in Fig. 1. These two multiplets arise from the olefinic and methylene protons, respectively. The spectrum of the purple solution of cyclopentadienylsodium, on the other hand, consists of only a single sharp peak due to the cyclopentadienyl anion. A mixture of sodium cyclopentadienide and cyclopentadiene shows an n.m.r. absorption that is a simple superposition of the spectra of the individual components. Similarly, the n.m.r. absorption of tropilidene, shown in Fig. 2, is not changed in any way on addition of tropylium fluoroborate to the solution, the tropylium ion resonance appearing in this spectrum as a single line. Thus there is evidence that proton exchange between the neutral molecules and their ions is extremely slow.

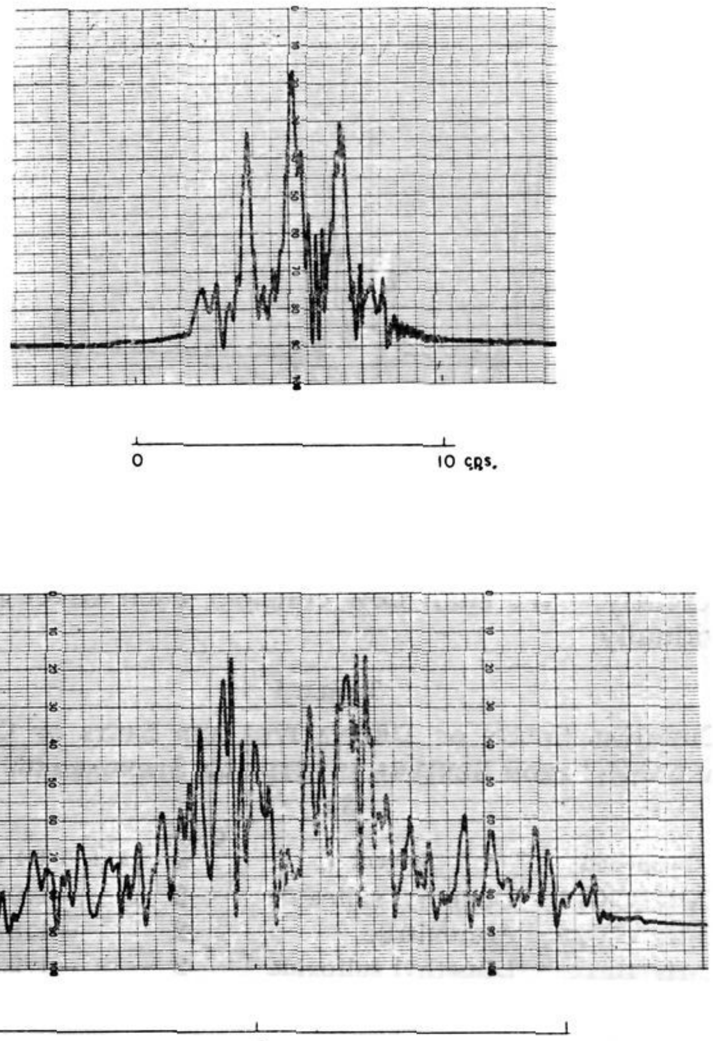

Fig. 1.—N.m.r. absorption of pure cyclopentadiene, 60 Mc., 29°: top, methylene hydrogens; bottom, olefinic hydrogens.

Table I lists the chemical shifts with respect to benzene as internal standard for several salts of $C_5H_5^-$ and $C_7H_7^+$. These solutions yield excellent n.m.r. spectra for the solvents and single-line resonances for each of the solutes. The line widths were solely determined by the homogeneity of the magnetic field. Using n.m.r. methods we were unable to detect any impurities in these solutions. Their concentrations, therefore, are estimated to be less than 5% of that of the main solute. For comparison Table I includes chemical shifts for three sandwich compounds—ferrocene, ruthenocene and osmocene—as well as magnesocene. The light color of our magnesocene solutions, as well as Wilkinson's conductivity measurements,[16] suggest that magnesocene is only partially dissociated in solution; therefore it is not considered to be a typical salt of $C_5H_5^-$. The chemical shift for $C_5H_5^-Na^+$ lies at +1.85 p.p.m. relative to benzene while those for the two tropylium salts in the same solvent appear at −1.9 p.p.m. Although the values depend slightly on the solvent and the accompanying ion, these variations are small; our values probably represent typical shifts for $C_5H_5^-$ and $C_7H_7^+$. Moreover, these results compare favorably with those of Leto, Cotton and Waugh,[15] who used a different solvent for $C_5H_5^-$ and $C_7H_7^+$ and obtained +2.0 and −2.0 p.p.m. for each of these species, respectively.

Discussion

There is no doubt that local charges have a most important effect on hydrogen shifts. There is a strong correlation between shifts and electronegativity, for example, in many saturated compounds.[20,21]

Table II lists several examples where the effect of charge on chemical shift may be isolated. Positive charge generally leads to lower screening for neighboring protons.

When a molecule is placed in a magnetic field, currents are set up in the molecule, and the additional magnetic field at the nucleus due to these currents causes an n.m.r. shift. Such currents flow (1)

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(18) G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. Nuclear Chem.*, **2**, 109 (1956).

(19) D. N. Kursanov and M. E. Vol'pin, *Doklady. Akad. Nauk, S.S.S.R.*, **113**, 339 (1957); *C. A.*, **51**, 14572e (1957). We are indebted to M. Feldman, University of California at Los Angeles, for the details of this preparation and for a sample of tropylium perchlorate.

(20) B. P. Dailey and J. N. Shoolery, THIS JOURNAL **77**, 3977 (1955).

(21) J. N. Shoolery, *J. Chem. Phys.*, **21**, 1899 (1953).

Fig. 2.—N.m.r. spectrum of pure cycloheptotriene, 60 Mc., 29°, shifts referred to benzene as internal standard; peaks due to the 5% impurity of toluene not shown.

around atoms, (2) within bonds and (3) from atom to atom around a ring. Each of these three types of currents can affect the ring hydrogen shifts differently. We shall now consider each effect individually.

Table I

Chemical Shifts of Derivatives and Salts of $C_5H_5^-$ and $C_7H_7^+$ from Benzene as Internal Standard (60 Mc., 30°)

Compound	Solvent	Concn., %	δ ± 0.004 p.p.m.
$C_7H_7^+ClO_4^-$	Dimethyl sulfoxide	2	−1.938
$C_7H_7^+ClO_4^-$	Acetonitrile	2	−1.873
$C_7H_7^+BF_4^-$	Dimethyl sulfoxide	2	−1.934
$C_7H_7^+BF_4^-$	Acetonitrile	2	−1.873
$C_5H_5^-Na^+$	Dimethyl sulfoxide	2	1.970
$C_5H_5^-Na^+$	Acetonitrile	2	1.785
$C_5H_5^-Na^+$	Tetrahydrofuran	2	1.724
$C_5H_5^-Li^+$	Tetrahydrofuran	2	1.738
$(C_5H_5)_2Mg$	Tetrahydrofuran	2	1.494
$(C_5H_5)_2Mg$	Ethyl ether	1	1.089
$(C_5H_5)_2Mg$	Benzene	1	0.819
$(C_5H_5)_2Mg$	Cyclohexane	1	1.185
$(C_5H_5)_2OS$	Tetrahydrofuran	2	2.696
$(C_5H_5)_2Ru$	Tetrahydrofuran	2	2.805
$(C_5H_5)_2Fe$	Tetrahydrofuran	2	3.200

Table II

Changes in Chemical Shift Following Alterations in Charge Distribution

Final state (A)	Initial state (B)	Proton	Shift (δ_{A-B} p.p.m.)
$CH_3NH_3^+$	CH_3NH_2	CH_3	−0.30[a]
$(CH_3)_2NH_2^+$	$(CH_3)_2NH$	CH_3	− .44[a]
$(CH_3)_3NH^+$	$(CH_3)_3N$	CH_3	− .70[a]
$NH_3^+CH_2CO_2^-$	$NH_2CH_2CO_2^-$	CH_2	− .29[b]
$\overset{+}{N}H_3CH_2CO_2H$	$\overset{+}{N}H_3CH_2CO_2^-$	CH_2	− .50[b]
$CH_3COHNHCH_3^+$	$CH_3CONHCH_3$	HCH_3	− .37[c]

[a] E. Grunwald, H. Loewenstein, and S. Meiboom, *J. Chem. Phys.* **27**, 641 (1957). [b] M. Takeda and O. Jardetzky, *ibid.*, **26**, 1346 (1957). [c] G. Fraenkel and C. Niemann, *Proc. Natl. Acad. Sci., U.S.* **44**, 688 (1958).

(1) The current flowing around the hydrogen atom itself depends mainly on the population of the hydrogen 1s orbital. In an isolated hydrogen atom the single 1s electron causes a shift of 17.8 p.p.m.,[22] while Pople[31] estimates a value of 21.4 p.p.m. for the contracted 1s orbital in the hydrogen molecule. Also, a strong electric field in the neighborhood of an isolated hydrogen atom distorts the 1s orbital and thus reduces the shielding from a single 1s electron. It has been proposed[23,24] that this distortion may appreciably affect the shielding independently of variations in electron density in the hydrogen 1s orbit; but the effect caused by the distortion is much too small to account for the relative shifts of $C_5H_5^-$ and $C_7H_7^+$. Moreover, this calcultion applies only to an isolated hydrogen atom.

The simplest way to estimate the shift caused by currents in the carbon atom of a C–H bond and in more distant groups is to replace the currents by point magnetic dipoles. The shift is then found to be proportional to the diamagnetic anisotropy constants of each atom.[7,9] The absolute value may be as large as 10 p.p.m. (*e.g.*, acetylene). but variations among ring hydrogen atoms is aromatic hydrocarbons are expected to be small since the diamagnetic anisotropy of each carbon atom is similar. Further, in alternant hydrocarbons, where the electron densities on carbon atoms are uniform, chemical shifts fit Pople's ring-current theory to an accuracy of ± 0.1 p.p.m.[25] This is indirect evidence that other currents are constant; however the diamagnetic anisotropy of an aromatic carbon atom may vary slightly with the local π-electron densities when these densities are not uniform. An electron in a 2pπ orbital has its greatest susceptibility perpendicular to the molecular plane; consequently the proton experiences *less shielding* with increasing electron density, which is contrary to our experimental observations. The field due to currents flowing on more distant atoms falls off as $1/R^3$ (where R is the distance) and, as it generally is much smaller than any local shielding, we shall neglect it.

(2) The paramagnetic current[7,26] flowing in the C–H bond arises from the excitation of an electron from the bonding to the antibonding C–H σ-orbital, and is probably almost the same for all C–H bonds.

(3) If the π-electrons in an aromatic ring could circulate freely, they would precess in a magnetic field with the Larmor angular velocity $\omega = eH/2mc$. Indeed, Pople's free electron model[5-7] with C–C and C–H bond lengths of 1.40 and 1.09 Å.[27] leads to ring-current shifts for $C_5H_5^-$ and $C_7H_7^+$ of +0.11 and −0.06 p.p.m., respectively, relative to benzene, whereas our average observed values are +1.85 and −1.90 p.p.m.

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[22] W. E. Lamb, *Phys. Rev.*, **60**, 817 (1941).

[23] T. W. Marshall and J. A. Pople, *Mol. Phys.*, **1**, 199 (1958).

[24] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

[25] H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc. (London)*, **A236**, 515 (1956).

[26] N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

[27] (a) V. Schomaker and L. Pauling, This Journal, **61**, 1769 (1939); (b) J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Cryst.*, **9**, 373 (1956); (c) A. B. Berndt, Ph.D. Thesis, California Institute of Technology, 1957; (d) E. S. Gould, *Acta Cryst.*, **8**, 657 (1955).

An alternative theory of the ring current[28,29] predicts slightly *different currents* in the five, six and seven-membered rings and shifts of −1.3, −1.75 and −2.14 p.p.m. for $C_5H_5^-$, C_6H_6 and $C_7H_7^+$, respectively; but this does not affect the inference that the observed shifts are not mainly due to ring currents. (Actually, the theory only gives the ratio of these shifts.)

An extremely important effect on the chemical shifts of hydrogens will result from the charge on the carbon atom to which the hydrogen is bonded. This charge effect includes the resulting changes of electron density on the hydrogen atom, the diamagnetic anisotropy of the carbon atom, and paramagnetic currents in the carbon C–H bond. All of these changes should be approximately proportional to the excess π-electron density q on the carbon atom. We suggest that the shift of an aromatic hydrogen is chiefly due to such charge effects following the formula

$$\delta(q) = aq \qquad (1)$$

where a is a constant. According to this assumption the charge shifts $\delta(q)$ of $C_5H_5^-$ and $C_7H_7^+$ relative to benzene should be $^1/_5a$ and $-^1/_7a$ compared to the shifts of +1.76 and −1.84 p.p.m. for $C_5H_5^-$ and $C_7H_7^+$, which remain after subtraction of the ring-current contribution calculated by Pople's method. If the relationship of eq. 1 holds, our chemical shifts show that a is in the region of +10 p.p.m./electron. We shall adopt this value provisionally.

At present it is not possible to tell whether or not the lack of strict proportionality is caused by special effects or should be regarded as evidence against eq. 1. More encouraging is the correlation[30] found between hydrogen shifts and theoretical electron densities in azulene. In the next section we estimate theoretically that the largest contribution to a is 5–7 p.p.m./electron. This arises from an increase of electron density on a hydrogen atom caused by polarization of the C–H bond by the excess charge on the carbon atom. The remaining portions of a cannot be calculated at present.

Polarization of the C–H Bond.—Suppose that a carbon atom C of an aromatic ring has an excess charge of $-q$ (q electrons) in the $2p_z$ atomic orbital (π). To determine how this affects the electron density on the C–H hydrogen atom, we assume that the two electrons in the C–H bond move in a carbon $2sp^2$ hybrid orbital (σ) or a hydrogen 1s orbital (h). The electrostatic field of the excess charge $-q$ than produces a potential energy difference V between the two ends of the bond and drives electrons out of σ into h. Clearly,

$$V = (K_{\pi\sigma} - K_{\pi h})$$

where $K_{\pi\sigma}$ and $K_{\pi h}$ are the Coulomb repulsion integrals

$$K_{\pi\sigma} = \iint \left|\sigma(\mathbf{r}_1)\right|^2 \frac{e^2}{r_{12}} \left|\pi(\mathbf{r}_2)\right|^2 d\mathbf{r}_1\, d\mathbf{r}_2$$

$$K_{\pi h} = \iint \left|h(\mathbf{r}_1)\right|^2 \frac{e^2}{r_{12}} \left|\pi(\mathbf{r}_2)\right|^2 d\mathbf{r}_1\, d\mathbf{r}_2$$

between an electron in π and an electron in σ or h. We form σ, π, and h from Slater atomic orbitals with nuclear charges of 3.25, 3.25 and 1.0, respectively. For a C–H bond length of 1.09 Å. this gives $K_{\pi\sigma}$ = 15.64 e.V., $K_{\pi h}$ = 9.49 eV., and V = 6.15 e.V.

To estimate the changes of electron density an assumption about the wave function of the C–H bond is necessary. We treat the C–H bond by simple molecular orbital theory, neglecting overlap. Then σ and h give rise to bonding and anti-bonding orbitals

$$\Sigma = \frac{1}{\sqrt{2}}(\sigma + h)$$

$$\Sigma^* = \frac{1}{\sqrt{2}}(\sigma - h)$$

In the ground state of the bond both electrons are in Σ with opposed spins, and their wave function is the Slater determinant

$$\Psi_0 = \left|\left|\, \Sigma\,(1)\; \Sigma\,(2) \,\right|\right| \alpha\beta$$

The effect of the electric field of the π electrons is to mix this state Ψ_0 with the excited state Ψ_1, in which one electron has been promoted to the anti-bonding orbital Σ^*

$$\Psi_1 = \left|\left|\, \Sigma\,(1)\; \Sigma^*(2) \,\right|\right| \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$$

When q is small we can treat the problem by first-order perturbation theory and write

$$\Psi = \Psi_0 + \lambda\Psi_1$$

with

$$\lambda = \frac{-qV}{(E_1 - E_0)\sqrt{2}}$$

The electron density ρ on the hydrogen atom then changes by an amount

$$\Delta\rho = \frac{qV}{E_1 - E_0} = \alpha q$$

which is proportional to q. The value of α depends on the excitation energy $(E_1 - E_0)$, which is probable within the range 15–30 e.V. This leads to α = 0.35 − 0.2. Taking 21.4 p.p.m.[31] for the shielding of one electron in a hydrogen 1s orbital we deduce that C–H bond polarization makes a contribution of 4–7 p.p.m./electron to a.

The σ–π interaction process described above has a superficial resemblance to the process responsible for isotropic hyperfine splittings by aromatic ring protons in radicals.[32] In reality, they are totally different: one involves the movement of charge, the other a rearrangement of electron spins.

The calculations show that the displacement of charge onto the C–H hydrogen has an important effect on chemical shifts for $C_5H_5^-$ and $C_7H_7^+$, but the approximations made permit only a rough estimate of this effect.

We shall now treat eq. 1 as an empirical relation for estimating electron densities in aromatic molecules from their observed proton shifts relative to benzene as internal standard, both substances being

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(28) H. London, *J. phys. Radium*, **8**, 397 (1937).

(29) J. A. Pople, *Mol. Phys.*, **1**, 175 (1958).

(30) W. G. Schneider, H. J. Bernstein and J. A. Pople, THIS JOURNAL, **80**, 3497 (1958).

(31) 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, p. 175

(32) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

present at low concentration and in a solvent that does not produce anomalous changes in shielding.[33,34] These estimates are compared in Table III with theoretical values from other sources.

The experimental charge distributions in Table III show all the features that are expected from the relative reactivities of the different positions. They also closely resemble the type of charge distribution predicted by the molecular orbital and resonance theories of aromatic molecules. Since the theoretical calculations are based on highly simplified assumptions and are not intended to provide accurate electron densities, it is not surprising that there are, at times, fairly large discrepancies between the calculated and "experimental" values. In particular, they involved assigning an "electronegativity parameter" to nitrogen and oxygen. A recent theoretical discussion[35] suggests that some of the work quoted here is based on too large a value for this parameter and may exaggerate the non-uniformity of the charge distribution.

TABLE III

CHARGE DENSITIES IN AROMATIC COMPOUNDS ESTIMATED FROM PROTON CHEMICAL SHIFTS

Compound	Excess electron density, q *ortho*	*meta*	*para*	Origin
Nitrobenzene	-0.097	-0.030	-0.042	Chemical shifts[a] and eq. 1
	$-.15$	$.00$	$-.17$	[b]
Aniline	$.077$	$.013$	$.040$	Chemical shifts and eq. 1
	$.02$	$.00$	$.02$	[b]
Pyridine	$-.13$	$.00$	$-.037$	Chemical shifts[d,e] and eq. 1
	$-.151$	$-.053$	$-.178$	[c]

[a] P. C. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956). [b] Molecular orbital calculations by G. W. Wheland and L. Pauling, *ibid.*, **57**, 2086 (1935). [c] Molecular orbital calculations by H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947). [d] Spectrum of 3% pyridine in CCl_4 taken in these laboratories. [e] Chemical shifts analyzed by W. G. Schneider, H. J. Bernstein and J. H. Pople, *Can. J. Chem.*, **35**, 1487 (1957).

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(33) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(34) A. A. Bothner-By and R. E. Glick, THIS JOURNAL, **78**, 1071 (1956).

(35) A. Lofthus, *Mol. Phys.*, **2**, 367 (1959).

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Stereochemistry of Allylic Rearrangements. XI. The Isomeric Rearrangement of *trans*-5-Methyl-2-cyclohexenyl *p*-Nitrobenzoate-carbonyl-O^{18} in Aqueous Acetone[1]

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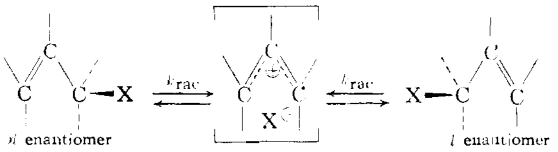
Optically active *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate undergoes simultaneous racemization and solvolysis in 80% acetone. The racemization is a stereospecific intramolecular isomeric allylic rearrangement—racemization is not accompanied by geometric isomerization or exchange with added *p*-nitrobenzoate ion. Carbonyl-O^{18} ester undergoes equilibration of the label between the two positions about twice as fast as it racemizes. Thus there is a path whereby the oxygen atoms become equivalent without loss of optical configuration. Presumably oxygen scrambling and racemization involve internal return. However, there must be more than one intermediate of this type: one which is common to the two enantiomers (involved in racemization and scrambling) and one which is not common to both enantiomers (involved in oxygen scrambling without racemization).

Introduction

Symmetrical allylic chlorides,[2] acid phthalates[3] and *p*-nitrobenzoates[4,5] undergo simultaneous racemization and solvolysis in hydroxylic solvents. The racemization, which accompanies solvolysis, results from an intramolecular stereospecific allylic rearrangement.[2-5] Presumably this process involves return from an internal ion pair intermediate I as



(1)

I

The solvolysis, which does not disturb the rearrangement (racemization), is not included in this scheme.

The preceding paper in this series describes an investigation of the relative positions of the oxygen atoms in the reactant and product for the rearrangement (racemization) of *trans*-α,γ-dimethylallyl *p*-nitrobenzoate in aqueous acetone.[5a] In that system it was found that carbonyl-O^{18} ester undergoes first-order equilibration of the label between the two positions at the same rate as active ester racemizes; *i.e.*, k_{eq} (eq. 2) is the same as k_{rac} (eq. 3).[5a,6]

$$dl\text{-ROCO}^{18}\text{C}_6\text{H}_4\text{NO}_2 \xrightarrow{k_{eq}} dl\text{-RO}^{18}\text{CO}^{18}\text{C}_6\text{H}_4\text{NO}_2 \quad (2)$$

$$\text{(active) ROCOC}_6\text{H}_4\text{NO}_2 \xrightarrow{k_{rac}} \text{(racemic) ROCOC}_6\text{H}_4\text{NO}_2 \quad (3)$$

With carbonyl-O^{18} optically pure (+)-ester it was shown that there is a tendency for the carbonyl-oxygen atom in the reactant (one enantiomer) to become the ether-oxygen atom in the product (the other enantiomer). If the reaction proceeded exclusively as summarized by II, k_{eq} would equal

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(2) H. L. Goering, T. D. Nevitt and E. F. Silversmith, THIS JOURNAL, **77**, 5026 (1955).

(3) (a) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 1129 (1955); (b) H. L. Goering and R. W. Greiner, *ibid.*, **79**, 3464 (1957).

(4) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 6249 (1955).

(5) (a) H. L. Goering and M. M. Pombo, *ibid.*, **82**, 2515 (1960); (b) H. L. Goering, *Rec. Chem. Prog.*, 109 (1960).

(6) M. M. Pombo, unpublished results.