c./sec. Once again it is not possible to say which of the pairs (4,7) and (5,6) give the signal at highest field.

It has not proved possible to give a detailed discussion of the interpretation of the relative chemical shifts for this molecule. In the first place, a complete assignment has not been made and, secondly, self-consistent charge densities are not available. However, the application of the ring model is again unsuccessful as it predicts too small a spread for the spectrum.

The dilution shifts for the individual signals were found to consist of a displacement to low field by about 1.7 p.p.m. for the 6- and 7-ring spectra, and 1.32 p.p.m. for the 5-ring spectrum. The general situation is therefore very similar to azulene, where the 7-membered ring shifted to low field more than the 5-ring, and a similar type of preferred molecular interaction between neighboring acepleiadylene molecules would have to be assumed. The crystal structure of acepleiadylene is not known.

One point of interest that arises from these two spectra concerns the relative values of the spin-coupling constants between neighboring protons in 5-, 6- and 7-membered aromatic rings. These differ considerably. For the 5-membered ring of azulene the coupling constant is only 3.5 c./sec. Small values are also found in other 5-membered ring molecules such as furan.[16] The values for 6-membered rings in various substituted benzenes[7,17] and naphthalene range around 6–8 c./sec. Finally all the values for 7-membered rings found in the present paper are in the region of 10–13 c./sec.

[16] Unpublished results.

[17] H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, THIS JOURNAL, **79**, 4596 (1957).

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A Simple Model for Calculating Magnetic Shielding of Nuclei in Molecules

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A simple formula for the nuclear magnetic shielding constant has been proposed. It has been applied to (a) the hydrogen molecule, (b) polynuclear aromatic hydrocarbons, (c) the "induced-current" model proposed by Pople and (d) effects of distant electrons localized to non-bonded atoms. The results obtained are quite satisfactory.

The general expression for the nuclear magnetic shielding constant σ has been given by Ramsey.[1] However, his expression is rather unpractical even for the simplest molecules and, therefore, a simpler expression[2] is desirable even if it is less rigorous. In the present paper, the simplification of Ramsey's expression is studied and the results are examined by numerical examples.

1. A Simple Expression for Nuclear Magnetic Shielding.—The nuclear magnetic shielding constant σ can be expressed[1] for real wave functions, using a second-order perturbation method, as

$$\sigma = (e^2/2mc^2)\left(0\right|\sum_k (x_k{}^2 + y_k{}^2)/r_k{}^3\left|0\right) - (e^2/m^2c^2)\sum_n{}'[1/(E_n - E_0)] \times \left[\left(0\right|\sum_k m_{zk}\left|n\right)\left(n\right|\sum_k m_{zk}/r^3{}_k\left|0\right)\right] \quad (1)$$

where x_k and y_k are the x and y coördinates of an kth electron, respectively, with the z-axis along an external magnetic field and the origin at the nucleus for which the shielding is desired, r_k the distance between the kth electron and the origin, and $\left(0\right|\sum_k m_{zk}\left|n\right)$ the matrix element between the molecular ground state and a molecular electronic state n of the orbital angular moment operator for the kth electron of $m_{zk} = (h/2\pi i)(x_k\partial/\partial y_k - y_k\partial/\partial x_k)$.

However, eq. 1 is difficult to apply since the wave functions of excited electronic states of molecules are seldom available. If $E_n - E_0$ is replaced by an average energy ΔE of the excited states, the expression can be reexpressed in a simpler form, involving only ground-state wave functions, as

$$\sigma = (e^2/2mc^2)\left(0\right|\sum_k (x_k{}^2 + y_k{}^2)/r_k{}^3\left|0\right) - (e^2/m^2c^2\cdot\Delta E)\left(0\right|\sum_k m_{zk}\cdot m_{zk}/r_k{}^3\left|0\right) \quad (2)$$

where the ground-state wave function is assumed to be real. Even eq. 2 is very difficult to evaluate.

However, the general relations[3]

$$(n|\partial/\partial x|0) = -m(2\pi/h)^2(E_n - E_0)(n|x|0)$$

and

$$(n|\partial/\partial y|0)] = -m(2\pi/h)^2(E_n - E_0)(n|y|0) \quad (3)$$

are found to be useful for simplifying eq. 2. Multiplying the both sides of the first of eq. 3 by

$$[(0|y^2\partial/r^3\partial x|n) - (0|xy\partial/r^3\partial y|n) - (0|x/r^3|n)]$$

and those of the second by

$$[(0|x^2\partial/r^3\partial y|n) - (0|xy\partial/r^3\partial x|n) - (0|y/r^3|n)]$$

and adding side by side, one has, upon summing over all excited states

$$(0|m_z\cdot m_z/r^3|0) = -m\sum_n{}'(E_n - E_0)[\{(0|y^2\partial/r^3\partial x|n) -$$

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

[2] Variational calculations of proton shifts have been reported by Das and Bersohn (*ibid.*, **104**, 849 (1956)) and by McGarvey (*J. Chem. Phys.*, **27**, 68 (1957)). The variational derivation of eq. 5 or 6 (see footnote 3) shows that these equations are of better approximation compared with Das and Bersohn's. McGarvey's treatment may be of better approximation than the present one but seems to be still too complicated to apply on such problems as discussed in b, c and d of the present paper.

[3] H. Eyring, J. Walter and G. Kimball, "Quantum Chemistry" John Wiley and Sons, Inc., New York, N. Y., 1944, p. 111.

$$(0|xy\partial/r^3\partial y|n) - (0|x/r^3|n)\}(n|x|0) + \{(0|x^2\partial/r^3\partial y|n) - (0|xy\partial/r^3\partial x|n) - (0|y/r^3|n)\}(n|y|0)] \quad (4)$$

If $E_n - E_0$ is replaced by ΔE, just as assumed in eq. 2, eqs. 4 and 2 give

$$\sigma = (e^2/2mc^2)\sum_k [(0|x_k^2 + y_k^2)/r_k^3|0) - (0|x_k/r_k^3|0)(0|x_k|0) - (0|y_k/r_k^3|0)(0|y_k|0)] \quad (5)$$

The mean value of eq. 5 σ_{av}, averaged over all orientations of a molecule, is given by

$$\sigma_{av} = (e^2/3mc^2)\sum_k [(0|1/r_k|0) - (0|x_k/r_k^3|0)(0|x_k|0) - (0|y_k/r_k^3|0)(0|y_k|0) - (0|z_k/r_k^3|0)(0|z_k|0)] \quad (6)$$

Equations 5 and 6 are, of course, of an approximate nature[4] and, therefore, their applicability to real molecules is examined in the following.

2. Applications. a. Hydrogen Molecule.—Equations 5 and 6 were applied to the hydrogen molecule using the molecular orbital wave function with the effective nuclear charge of 1.197 at the equilibrium position.[5] The results obtained are shown in Table I. The value of σ_{av}, 2.67×10^{-5}, is to be compared with the value[1] 2.68×10^{-5}, rather than[6] 2.66×10^{-5}, and that of the paramagnetic term of eq. 6 -0.55×10^{-5} with the value[1] -0.56×10^{-5} found from a combination of theory and experiment. The agreement is quite satisfactory.

TABLE I

THE NUCLEAR MAGNETIC SHIELDING CONSTANTS OF THE HYDROGEN MOLECULE[a] CALCULATED FROM EQS. 5 AND 6

	Diamag. term	Paramag. term	Sum
$\sigma_{av} \times 10^5$	3.22	−0.55	2.67
$\sigma_{\parallel} \times 10^5$	2.88	0	2.88
$\sigma_{\perp} \times 10^5$	3.39	−0.83	2.56

[a] σ_{av}, mean nuclear magnetic shielding constant; $\sigma_{\parallel}$, nuclear magnetic shielding constant with an external magnetic field parallel to the molecular axis; $\sigma_{\perp}$, nuclear magnetic shielding constant with an external magnetic field perpendicular to the molecular axis.

b. The Chemical Shifts Due to the Delocalized Nature of π-Electrons.—Recently it has been shown[7,8] by Bernstein, Schneider and Pople that the protons in aromatic hydrocarbons are magnetically non-equivalent. These spectra were explained[8,9] in terms of the interaction between a proton magnetic moment and diamagnetic currents induced in aromatic rings by an external magnetic field applied perpendicular to a molecular plane ("induced-current" model). In this section, the same subject is discussed by the use of eq. 5. Corresponding to the "induced-current" model, only a component of an external magnetic field perpendicular to a molecular plane is taken into account and the contribution from the delocalized nature of π-electrons to σ is considered. Using LCAO wave functions for a π-electron system and summing over all orientations of a molecule, eq. 5 gives, for a molecule having a center of symmetry

$$\sigma_{av} = (e^2/6mc^2)\sum_i q_i[(\varphi_i|(x^2 + y^2)/r^3|\varphi_i) - (\varphi_i|x/r^3|\varphi_i)x_0 - (\varphi_i|y/r^3|\varphi_i)y_0] \quad (7)$$

where x, y, x_0, y_0, measured from the origin at the nucleus for which the shielding is desired, are the x and y coördinates of an electron and those of the center of a molecule, respectively, r the distance between the origin and an electron, and q_i and φ_i the π-electron charge density at and the p_π wave function of an ith carbon atom, respectively. Equation 7 involves not only the contribution from the delocalized nature of π-electrons but also that from the electrons localized to each atomic p_π orbital. The latter is given by

$$(e^2/6mc^2)\sum_i q_i[(\varphi_i|(x^2 + y^2)/r^3|\varphi_i) - (\varphi_i|X_i/r^3|\varphi_i)R_i] \quad (8)$$

where X_i is the coördinate of an electron measured along the axis directed from the origin to an ith carbon atom and R_i the distance between the origin and the ith carbon atom. Subtracting eq. 8 from eq. 7, the shielding constant σ_{av}(deloc.) arising from the delocalized nature of π-electrons is given by

$$\sigma_{av}(\text{deloc.}) = -(e^2/6mc^2)\sum_i q_i[(\varphi_i|x/r^3|\varphi_i)x_0 + (\varphi_i|y/r^3|\varphi_i)y_i - (\varphi_i|X_i/r^3|\varphi_i)R_i] \quad (9)$$

Equation 9, which must be the quantum-mechanical expression of the "induced-current" model, is applied to benzene and polycyclic aromatic hydrocarbons. The shielding constant for the latter is calculated as the sum of those arising from each benzene nucleus. The chemical shifts calculated for a fixed frequency of 40 *M*c./sec., with $r_{C-H} = 1.08$ Å. and $r_{C-C} = 1.40$ Å., are given in Table II. Slater-type wave functions with the effective nuclear charge 3.25 are used.

In Table II, the essential agreement between the present results and those from the "induced-current" model, which is capable of reproducing the main features of the n.m.r. spectra of aromatic hydrocarbons, is shown.

c. The Derivation of the "Induced-current" Model.—The successful results shown in section b suggest that the original form of the "induced-current" model may be derived from eq. 5. Suppose that a benzene nucleus is represented by a ring as shown in Fig. 1 and each of π-electrons of benzene is distributed homogeneously on the ring. Then, eq. 5 applied to the π-electron system of benzene gives, with an external magnetic field perpendicular to the molecular plane

$$\sigma = (3e^2/mc^2)[\overline{(1/r)} - \overline{(x/r^3)}R] \quad (10)$$

where r, x and R are denoted in Fig. 1 and the average is taken along the circumference of the ring. The integrals are obtained readily as

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(4) Equation 5 is also derivable by the use of the variation function $\varphi_0(1 + A(ax + by))$, where φ_0 is the unperturbed wave function, and A, a and b are the variable parameters. This function can be shown to be essentially equivalent to that used by F. London (*J. phys. rad.*, **8**, 397 (1937)) for calculating the diamagnetic anisotropy of polynuclear aromatic hydrocarbons. These treatments will be discussed separately elsewhere.

(5) C. A. Coulson, *Trans. Faraday Soc.*, **33**, 1479 (1937).

(6) G. F. Newell, *Phys. Rev.*, **80**, 476 (1950).

(7) H. J. Bernstein and W. G. Schneider, *J. Chem. Phys.*, **24**, 468 (1956).

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

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

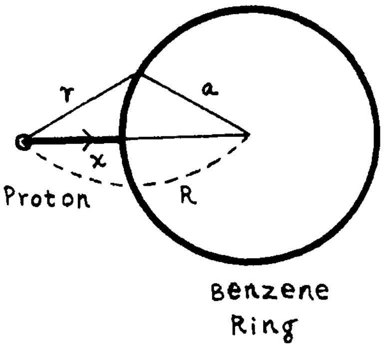

Fig. 1.—The schematical representation of the benzene molecule.

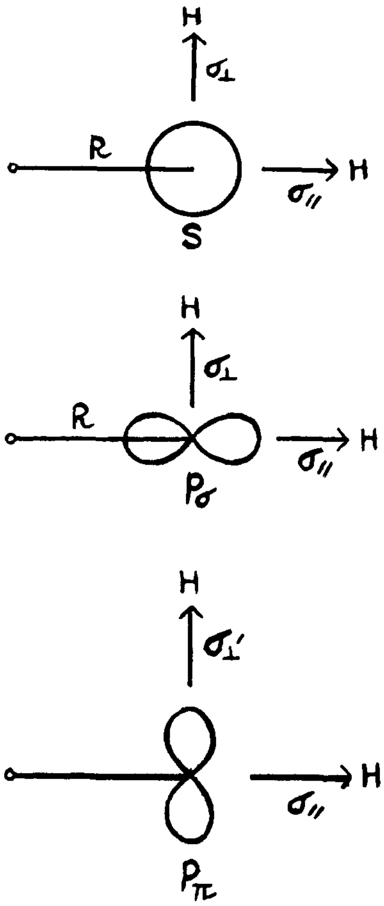

Fig. 2.—The definitions of $\sigma_{//}$ and $\sigma\perp$ in Table III.

$$\overline{(1/r)} = (1/R) + (1/4)(a^2/R^3) + (9/64)(a^4/R^5) + \ldots \quad (11)$$

and

$$\overline{(x/r^3)} = (1/R) + (3/4)(a^2/R^3) + (45/64)(a^4/R^5) + \ldots \quad (12)$$

Substituting eqs. 11 and 12 into 10, and averaging over all orientations of a molecule, gives

$$\sigma_{\text{av}} = -(e^2/2mc^2)[(a^2/R^3) + (9/8)(a^4/R^5) + \ldots] \quad (13)$$

The first term of eq. 13 gives the "induced-current" model used by Bernstein, *et al.*, and the second the correction for it.

d. Effects of Distant Electrons Localized to Non-bonded Atoms.—Recently it has been considered that electrons localized to atoms relatively far removed from the nucleus in question may make an appreciable contribution to σ.[10] Such effects can be formulated easily by introducing a proper wave function of each electron into eq. 5 or 6. Using Slater-type wave function for each electron, the shielding constant due to an electron centered on the point removed by R from the given nucleus can be expressed, in general, as

$$\sigma = (e^2/2mc^2)(1/\zeta^4R^5)[A_0 + A_2(\zeta R)^2 + e^{-2\zeta R}\{a_0 + a_1(\zeta R) + \ldots + a_n(\zeta R)^n\}] \quad (14)$$

where ζ is an effective nuclear charge divided by an effective quantum number. In Table III are listed the values of the A's and a's for 1s, 2s, $2p_\sigma$, $2p\pi$, 3s, $3p_\sigma$ and $3p\pi$ electrons. The definitions of $\sigma_{||}$, and $\sigma_\perp$ are given in Fig. 2. The results given in Table III can be checked by the relations

$$\sigma_{\text{av}} = (1/3)(\sigma_{||} + 2\sigma_\perp)$$
$$\sigma_{\text{av}} = (1/3)(\sigma_{||} + \sigma_\perp' + \sigma_\perp)$$
$$\sigma_{\text{av}}\,(\text{ns}) = (1/3)[\sigma_{\text{av}}(\text{np}_\sigma) + 2\sigma_{\text{av}}(\text{np}_\pi)]$$

which have to hold among σ's.

The shielding constant arising from electrons localized to a halogen atom is calculated as $+0.17 \times 10^{-6}$ and $+0.36 \times 10^{-6}$ for CH_3F and CH_3Cl, respectively, assuming pure covalent character for C–halogen bonds. If some amount of ionicity is introduced for the bonds, these values get smaller. The corresponding values estimated by McConnell are $\pm 0.1 \times 10^{-6}$ and $\pm 0.3 \times 10^{-6}$, respectively. For non-alternant hydrocarbons as azulene,[8] effects of non-homogeneous charge distributions of rings on proton shifts may be treated in the same way. It would be worth noting that electrons in s orbital or in closed shell configuration have, as shown in Table III, only negligibly small contri-

TABLE II

CHEMICAL SHIFT CALCULATED WITH EQ. 9

Compound	Position[a]	Calcd. chem. shift (c./sec.) Induced-current model[b]	Present model
Benzene		−73	−86
Naphthalene	1	−99	−112
	2	−83	−96
Anthracene	9	−126	−136
	1	−106	−119
	2	−86	−99
Phenanthrene	4	−122	−133
	9	−109	−123
	1	−105	−118
	3	−88	−102
	2	−87	−100
Pyrene	3	−120	−133
	2	−115	−128
	1	−97	−111
Triphenylene	1	−127	−139
	2	−92	−106
Perylene	1	−139	−151
	3	−116	−130
	2	−102	−116

[a] The numbering of positions is the same as that used in ref. 7. [b] Recalculated with the same molecular constants as those used in the present model.

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

TABLE III

COEFFICIENTS IN EQ. 14[a]

Orbital		A_0	A_2	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}
1s	∥		2			−2	−4	−4	−2					
	⊥		−1			1	2	2	2	2				
	av								2/3	4/3				
2s	∥		5			−5	−10	−10	−19/3	−8/3	−2/3			
	⊥		−5/2			5/2	5	5	11/3	7/3	4/3	2/3		
	av								1/3	2/3	2/3	4/9		
2pσ	∥	72	3	−72	−144	−147	−102	−54	−23	−8	−2			
	⊥	−36	−15/2	36	72	159/2	63	39	20	9	4	2		
	av		−4			4	8	8	17/3	10/3	2	4/3		
2pπ	∥	−36	6	36	72	66	36	12	2					
	⊥′	27	−3/2	−27	−54	−105/2	−33	−15	−5	−1				
	⊥″	9	3/2	−9	−18	−39/2	−15	−9	−4	−1				
	av		2			−2	−4	−4	−7/3	−2/3				
3s	av								2/9	4/9	4/9	8/27	4/27	8/135
3pσ	av		−112/15			112/15	224/15	224/15	458/45	244/45	112/45	16/15	4/9	8/45
3pπ	av		56/15			−56/15	−112/15	−112/15	−214/45	−92/45	−26/45	−4/45		

[a] The definitions of $\rho_{\parallel}$ and $\rho_{\perp}$ are given in Fig. 2.

butions on σ_{av}, just as expected from a classical model.

As shown in sections a, b, c and d, eq. 5 and 6 give quite satisfactory results for real cases. Therefore, these equations may be considered to be fairly general in spite of the approximate nature of the derivation and to be useful, because of their simplicity, also for other cases in the same field.

NAGOYA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Electric Moments of Organic Peroxides. I. Dialkyl Peroxides, Alkyl Hydroperoxides and Diacyl Peroxides[1]

BY WALTER LOBUNEZ, JAMES R. RITTENHOUSE AND JOHN G. MILLER

RECEIVED FEBRUARY 4, 1958

The electric moments of a group of dialkyl peroxides, alkyl hydroperoxides and diacyl peroxides have been measured in benzene at temperatures in the range 20–50°. The observed moments agree with those calculated for fixed skew configurations about the peroxy grouping as in the Penney–Sutherland structure for hydrogen peroxide. In the diacyl peroxides, both of the carbonyl groups appear to face inward.

At present the most widely accepted model for the configuration of hydrogen peroxide is that proposed by Penney and Sutherland.[2] Practically all of the infrared and Raman spectral data have been correlated with this fixed skew structure[3] and the dipole moment[4] of this substance as well as the X-ray investigations of the crystalline[5a] and liquid[5b] material support this model.

Recently, Rogers and Campbell[6] have shown that di-*t*-butyl peroxide and *t*-butyl hydroperoxide have dipole moments in accord with hydrogen peroxide-like structures and that the bulk of the *t*-butyl groups appears to exert a steric effect upon the magnitude of the dihedral angle between the C–O–O planes in the dialkyl peroxide. Shortly before the publication of this work by Rogers and Campbell, an investigation of the dipole moments of some of the principal classes of organic peroxides was started here. This article reports the results for some dialkyl peroxides, alkyl hydroperoxides and diacyl peroxides.

Experimental

Preparation of Materials. Benzene.—Thiophene-free benzene was stored above sodium and refluxed over sodium shortly before use. It was then distilled with discard of the first portions of the distillate.

Di-*t*-butyl Peroxide.—A gift sample from the Shell Chemical Corporation was distilled at 98.5 mm. The fraction boiling at 52.5° was used. This was the major part of the distillate and had the refractive index $n^{30}D$ 1.3841.

***n*-Butyl *t*-Butyl Peroxide.**—This compound was synthesized by the method of Rust, Seubold and Vaughan.[7] It was fractionated *in vacuo*. The middle fraction, b.p. 53° (30 mm.), was used in the measurements.

***t*-Butyl Hydroperoxide.**—Material from the Lucidol Division of the Novadel-Agene Corporation was fractionally distilled. The large fraction, comprising most of the material, b.p. 51.8° (40 mm.), $n^{30}D$ 1.3958, was used for the measurements. A lower boiling fraction, b.p. 47–49.5° (52 mm.), was taken for separate measurement to duplicate the material (b.p. 45° at 40 mm.) used by Rogers and Campbell.[6]

Cumene Hydroperoxide.—A sample of 98% pure cumene hydroperoxide in petroleum ether was donated by the Hercules Powder Company through the courtesy of Dr. John

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[1] A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Eastern Utilization Research and Development Division of the Agricultural Research Service. Part of this work was presented at the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, February 1956.

[2] W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

[3] O. Bain and P. A. Giguere, *Can. J. Chem.*, **33**, 527 (1955).

[4] E. P. Linton and O. Maass, *Can. J. Research*, **7**, 81 (1932).

[5] (a) S. C. Abrahams, R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 15 (1951); (b) J. T. Randall, *Proc. Roy. Soc.* (*London*), **159**, 82 (1937).

[6] M. T. Rogers and T. W. Campbell, THIS JOURNAL, **74**, 4742 (1952).

[7] F. F. Rust, F. H. Seubold and W. E. Vaughan, *ibid.*, **72**, 338 (1950).