A Technique for Determining Proton Chemical Shifts arising from Ring Current Effects: the Conformations of Triply Ortho-substituted Diphenyl Ethers¹

J. J. BERGMAN AND W. D. CHANDLER

Department of Chemistry, University of Saskatchewan, Regina, Saskatchewan

AND

R. Y. MOIR

Department of Chemistry, Queen's University, Kingston, Ontario Received July 22, 1970

A double-difference technique, making it possible to obtain that part of proton chemical shifts that originates in the shielding by the second ring in diphenyl compounds, is discussed. Evidence in support of the theory comes from the chemical shifts of aromatic ring protons in a family of triply ortho-substituted diphenyl ethers. The conformations of these ethers appear to be independent of the ortho-substituent, X (X \neq H), and the COC angle is shown to be approximately 120°.

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Studies of aromatic conformation rely heavily upon the magnetic anisotropy of the benzene ring. Separation of this effect from the others that influence the chemical shift of proton magnetic resonance (p.m.r.) signals has been difficult, and most of the previous studies (*e.g.*, ref. 1) have been content with qualitative or empirical evaluations. This paper describes a method for determining the "other ring" contribution quantitatively for diphenyl ethers.

In a previous paper (1) it was shown by nuclear magnetic resonance (n.m.r.) spectral analysis that triply ortho-substituted diphenyl ethers derived from metameconine (1*a*-*c*) adopt the asymmetric, "H_a-inside" conformation as their principal conformation (Fig. 1). This conclusion was inferred from the observation that the n.m.r. signal from H_a occurs 0.27 to 0.38 p.p.m. to higher field in the diphenyl ethers than in the corresponding anisoles (2*a*-*c*). At the same time, the signals from H_b and H_c are 0.13 to 0.18 and 0.067 to 0.20 p.p.m. to higher and lower field respec-



FIG. 1. "H_a-inside" conformation of triply orthosubstituted diphenyl ethers derived from metameconine.

¹Much of this work is taken from the Ph.D. Thesis of W. D. Chandler, Queen's University, Kingston, August 1965 and was presented at the National Meeting of the Chemical Institute of Canada, in Montreal, June, 1965.

 $\begin{array}{c} CH_{3}O \\ CH_{3}O \\ CH_{3}O \\ H_{a} \\ H_{b} \\ H_{c} \\ COOCH_{3} \\ 1 \\ 1a: X = NO_{2}; 1b: X = NH_{2} \\ 1c: X = I; 1d: X = H \end{array}$

tively when a similar comparison is made. H_a and H_b must see more of the ring current-induced shielding field of the metameconine ring than does H_c and the " H_a -inside" conformation of Fig. 1 accounts for this fact nicely. It was shown in the same paper that the two ortho-hydrogens of 1d are magnetically equivalent, indicating that the two "H-inside" conformations are exchanged at such a rate that the average lifetime is less than the lifetime of proton spin states.

In theory, it should be possible to determine the average conformation with greater precision than



was done in the previous work, since the "otherring" shielding is highly conformation dependent. The conformation, or geometrical relationship of the two rings, can, except for the carbon-oxygen bond lengths, be described in terms of three angular parameters. These are the COC bond angle and the two angles defining the rotation of each ring relative to the plane containing the COC bond. Every conformation will fix the geometric relation of H_a , H_b , and H_c to the other ring and, by the use of some appropriate model (2-5), the "other-ring" shielding at these protons could be calculated. If, at the same time, there were a method of extracting the "other-ring" shielding for each of H_a , H_b , and H_c from their chemical shifts, these experimental values could be related to the calculated ones and the average conformation deduced. There would be three equations, one for each of the three protons, to calculate the three unknown angles. In practice, such a procedure would be difficult for two reasons: (i) the "other-ring" shielding must be averaged over weighted values of the angles as the n.m.r. spectrum is obtained for a mobile system. Doing this averaging could be a formidable task unless reasonable guesses were made as to the limits to be imposed on the angles; (ii) the total chemical shift is dependent upon a number of factors, the magnetic anisotropy of the second ring being only one of them.

The next section describes a method of extracting the "other-ring" effects from experimental chemical shifts.

First-order, Double-difference Method

The discussion is restricted to the determination of "other-ring" effects for protons of triply ortho-substituted diphenyl ethers such as 1a-1c. Our method requires that the related disubstituted ether (1d) and anisoles (2a-2d) be available for comparison.

Let δ_{DX}^{j} be the chemical shift observed for the *j*th ring proton (H_a, H_b, or H_c) in a diphenyl ether such as 1*a*-1*c*, *i.e.* with X not hydrogen. The simplest possible theory would be that this chemical shift could be thought of as made up of independent contributions from: (*i*) the substituent X, δ_X^{j} , (*ii*) the rest of the molecule but not including "other-ring" shielding, δ_D^{j} , and (*iii*) the "other-ring" shielding, $\delta_{\omega X}^{j}$, which depends on conformation. Thus,

$$\delta_{\mathrm{DX}}{}^{j} = \delta_{\mathrm{X}}{}^{j} + \delta_{\mathrm{D}}{}^{j} + \delta_{\omega\mathrm{X}}{}^{j}$$

In practice this model was found to work well enough to inspire confidence in the approach, but considerable improvement was obtained by the introduction of a parameter $\delta_{D,X}{}^{j}$, which expresses the fact that the contributions of D and X are not quite independent. With this term added the working equation is [1].

1]
$$\delta_{\mathrm{DX}}{}^{j} = \delta_{\mathrm{D}}{}^{j} + \delta_{\mathrm{X}}{}^{j} + \delta_{\mathrm{D},\mathrm{X}}{}^{j} + \delta_{\omega\mathrm{X}}{}^{j}$$

As shown later this very simple model satisfied several experimental tests. For the anisoles such as 2a-2c

$$[2] \qquad \qquad \delta_{AX}{}^{j} = \delta_{A}{}^{j} + \delta_{X}{}^{j} + \delta_{A,X}{}^{j}$$

where $\delta_{AX}{}^{j}$ is the chemical shift of the *j*th proton in the appropriately substituted anisole. Subtracting [2] from [1] for the same X and *j* gives

$$\begin{bmatrix} 3 \end{bmatrix} \quad \delta_{\mathrm{DX}}{}^{j} - \delta_{\mathrm{AX}}{}^{j} = (\delta_{\mathrm{D}}{}^{j} - \delta_{\mathrm{A}}{}^{j}) \\ + (\delta_{\mathrm{D,X}}{}^{j} - \delta_{\mathrm{A,X}}{}^{j}) + \delta_{\omega\mathrm{X}}{}^{j}$$

When X = H(1d and 2d) eq. 3 becomes

[4]
$$\delta_{\mathrm{DH}}{}^{j} - \delta_{\mathrm{AH}}{}^{j} = (\delta_{\mathrm{D}}{}^{j} - \delta_{\mathrm{A}}{}^{j}) + (\delta_{\mathrm{D,H}}{}^{j} - \delta_{\mathrm{A,H}}{}^{j}) + \delta_{\omega\mathrm{H}}{}^{j}$$

The difference between [3] and [4] gives the double-difference eq. 5.

$$\begin{aligned} [5] \quad \Delta_{\mathbf{X}}{}^{j} &\equiv (\delta_{\mathbf{D}\mathbf{X}}{}^{j} - \delta_{\mathbf{A}\mathbf{X}}{}^{j}) - (\delta_{\mathbf{D}\mathbf{H}}{}^{j} - \delta_{\mathbf{A}\mathbf{H}}{}^{j}) \\ &= (\delta_{\mathbf{D},\mathbf{X}}{}^{j} - \delta_{\mathbf{A},\mathbf{X}}{}^{j}) - (\delta_{\mathbf{D},\mathbf{H}}{}^{j} - \delta_{\mathbf{A},\mathbf{H}}{}^{j}) \\ &+ (\delta_{\omega\mathbf{X}}{}^{j} - \delta_{\omega\mathbf{H}}{}^{j}) \end{aligned}$$

Were it not for the two non-linear terms, Δ_X^j would be a direct experimental measure of the difference in "other-ring" shielding for diphenyl ethers with X = H and $X \neq H$, and if the assumption were made that $\delta_{\omega X}^j$ is independent of the substituent X, then eq. 5 would predict Δ_X^j to be a constant throughout a given family. Although the number of compounds in family 1 was limited, the observation (1) that Δ_X^j varies with X far beyond experimental error suggests that $\delta_{\omega X}^j$ is not substituent independent, or that the non-linear terms are important or both.

Equation 5 may be further simplified if use is made of the separability postulate.² The interaction shifts are written as

$$\delta_{\mathbf{Y},\mathbf{Z}^{j}} = I_{\mathbf{Y}^{j}}I_{\mathbf{Z}^{j}}$$

[6]

 ^{2}A discussion of this postulate is given by Leffler and Grunwald (6) under the theory of extrathermodynamic relationships.

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the product of separate parameters for each part, provided that the interaction is small or has a direction that remains approximately constant for the family to be compared. Then eq. 5 becomes

[7]
$$\Delta_{X}{}^{j} = (I_{D}{}^{j}I_{X}{}^{j} - I_{A}{}^{j}I_{X}{}^{j}) - (I_{D}{}^{j}I_{H}{}^{j} - I_{A}{}^{j}I_{H}{}^{j}) + (\delta_{\omega X}{}^{j} - \delta_{\omega H}{}^{j})$$

[8] $\Delta_{X}{}^{j} = (I_{X}{}^{j} - I_{H}{}^{j})(I_{D}{}^{j} - I_{A}{}^{j})$

 $+ (\delta_{\omega \mathbf{x}}{}^j - \delta_{\omega \mathbf{H}}{}^j)$

The use of [8] is made difficult by the two X-dependent terms on the right side. However, if $\delta_{\omega X}{}^{j}$ were independent of X (X \neq H), a plot of $\Delta_{X}{}^{j}$ vs. $I_{X}{}^{j} - I_{H}{}^{j}$ would result in a straight line whose intercept on the $\Delta_{X}{}^{j}$ axis would be the desired $\delta_{\omega X}{}^{j} - \delta_{\omega H}{}^{j}$ for a mythical diphenyl ether with the same conformation as the other ethers $(X \neq H)$ but for which the electronic properties of X would be the same as those of H. The problem with this analysis is that the interaction parameters $I_{\mathbf{X}}^{j}$ are not known.

There have been attempts to correlate the chemical shifts of aromatic protons with substituent parameters such as Hammett's o values (7), and d values of Martin and Dailey (8), and Qvalues (9-11).³ Since all of these parameters have been used to explain non-additive chemical shifts with some success, it is not unreasonable to assume that the I_X^{j} parameters might be related in some way to them. If a linear relationship were to hold, the following equations would be obtained.

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$$\begin{bmatrix} 9 \end{bmatrix} \quad \Delta_{\mathbf{X}}^{a} = A(d_{m}^{\mathbf{X}} - d_{m}^{\mathbf{H}}) + (\delta_{\omega \mathbf{X}}^{a} - \delta_{\omega \mathbf{H}}^{a}) \\ \Delta_{\mathbf{X}}^{a} = B(\sigma_{m}^{\mathbf{X}} - \sigma_{m}^{\mathbf{H}}) + (\delta_{\omega \mathbf{X}}^{a} - \delta_{\omega \mathbf{H}}^{a}) \end{bmatrix}$$

[10]
$$\Delta_{\mathbf{X}}^{\ b} = C(d_{p}^{\ X} - d_{p}^{\ H}) + (\delta_{\omega \mathbf{X}}^{\ b} - \delta_{\omega \mathbf{H}}^{\ b})$$
$$\Delta_{\mathbf{X}}^{\ b} = D(\sigma_{p}^{\ X} - \sigma_{p}^{\ H}) + (\delta_{\omega \mathbf{X}}^{\ b} - \delta_{\omega \mathbf{H}}^{\ b})$$

[11]
$$\Delta_{\mathbf{X}}^{\ c} = F(d_o^{\ X} - d_o^{\ H}) + (\delta_{\omega \mathbf{X}}^{\ c} - \delta_{\omega \mathbf{H}}^{\ c})$$
$$\Delta_{\mathbf{X}}^{\ c} = G(Q^{\mathbf{X}} - Q^{\mathbf{H}}) + (\delta_{\omega \mathbf{X}}^{\ c} - \delta_{\omega \mathbf{H}}^{\ c})$$

where A, B, C, D, E, F, and G are all constants. Since the σ , d, and Q parameters are known or can be calculated, an experimental way is open to test the double-difference theory and its underlying assumptions and, at the same time, to obtain "other-ring" shielding data.

Results

To test the method outlined above a new series of triply ortho-substituted diphenyl ethers (3) was prepared. This particular series was chosen because (i) it was easier to synthesize than the corresponding metameconine series (1) and (ii) the two trichlorophenyl ring protons are equivalent, can easily be identified, and their signal does not interfere with the ABC pattern of the other three aromatic protons.



The n.m.r. spectrum of each ether was taken along with that of the corresponding anisole (2) at ambient temperature. In all cases concentration effects were minimized. To insure accuracy of the chemical shift data, the aromatic region of each spectrum was reproduced to within ± 0.2 Hz by an ABC or AA'BB' calculation. The experimental values for Δ_x^{j} are given in Table 1.

An excellent linear, least-squares correlation was obtained from a plot⁴ of $\Delta_{\mathbf{X}}^{b}$ against σ_{p} (Fig. 2), with a standard deviation of 0.005 p.p.m.

TABLE 1. Δ_{x}^{j} values for the diphenyl ether series 3*

 X	$\Delta_{\mathbf{x}^{a}}$ (p.p.m.)†	$\Delta_{\mathbf{x}}^{b}$ (p.p.m.)†	$\Delta_{\mathbf{x}^{c}}$ (p.p.m.)†
NO ₂ NH ₂ I CN Cl OCH ₃	$\begin{array}{r} -0.419 \ddagger \\ -0.408 \\ -0.398 \\ -0.375 \\ -0.402 \\ -0.382 \end{array}$	$\begin{array}{r} -0.107 \\ -0.167 \\ -0.140 \\ -0.110 \\ -0.132 \\ -0.143 \end{array}$	0.165 0.118 0.097 0.128 0.112 0.132

*In solution in chloroform-d. †The estimated experimental error is ± 0.007 p.p.m. ‡The δ values were measured relative to tetramethylsilane so as to increase as the applied magnetic field decreases. The negative sign indicates that H_a and H_b are more shielded in the diphenyl ether than in the corresponding anisole.

 $^{4}\sigma$ values have been taken from reviews by Jaffé (12) and Ritchie and Sager (13).

³W. B. Smith, private communication. For purposes of this work the Q values for NH₂ and NO₂ were taken to be -0.7 and 6.3, respectively (11).

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FIG. 2. Plot of $\Delta_{\mathbf{X}}^{b}$ vs. σ_{p} .

and a correlation coefficient of 0.97. Using $\sigma_p^{\rm H} = 0.00$ and the equation for the line $(\Delta_{\rm X}^{\ b} = -0.149 + 0.0395\sigma_p^{\rm X})$, $\delta_{\omega \rm X}^{\ b} - \delta_{\omega \rm H}^{\ b}$ was calculated to be -0.140 ± 0.002 p.p.m., well within the estimated experimental error. By comparison, the average value, $\bar{\Delta}_{\rm X}^{\ b}$, for the six compounds studied is -0.133 p.p.m. with a standard deviation of 0.020 p.p.m. As expected, the correlation between $\Delta_{\rm X}^{\ b}$ and d_p was equally good, since d_p and σ_p themselves correlate well (8). It would seem that there is an experimental justification for the approach used for H_b.

There is a poorer correlation between $\Delta_{\mathbf{x}}^{c}$ and Q (Fig. 3) or d_o with the points for X = I and X = Cl deviating from the best straight line drawn for the other four substituents by 0.03 to 0.05 p.p.m. Without these two points the standard deviation is 0.010 p.p.m. and the correlation coefficient is 0.89. Using the known value for $Q^{\rm H}$, $\delta_{\omega X}{}^c - \delta_{\omega H}{}^c$ was calculated to be 0.135 \pm 0.003 p.p.m., again within experimental error. With all six points included, the standard deviation increased to 0.018 p.p.m. while $\delta_{\omega X}^{c} - \delta_{\omega H}^{c}$ was 0.123 ± 0.008 p.p.m. The average value for the six compounds is 0.125 p.p.m. with a standard deviation of 0.023 p.p.m. The inability of substituent parameters to account for the chemical shifts of protons ortho to I and, to a lesser extent,

to Cl, is well known (7, 8). However, the present deviation of 0.05 p.p.m. is lower than that observed by these single-difference techniques. In light of the earlier work on substituent parameters, it is surprising that the CN group does not also cause a large deviation.

 $\Delta_{\mathbf{X}}^{a}$ does not correlate with either σ_{m} (Fig. 4) or d_{m} within experimental error although there is a trend of $\Delta_{\mathbf{X}}^{a}$ becoming slightly less negative with decreasing σ_{m} and with increasing d_{m} . The standard deviation from a straight line is 0.018 p.p.m. with a correlation coefficient of 0.06. By comparison, the average value $\overline{\Delta}_{\mathbf{X}}^{a} = -0.396$ p.p.m. with a standard deviation of 0.017 p.p.m. It is this average value that will be used in subsequent discussion of $\delta_{\omega \mathbf{X}}^{a} - \delta_{\omega \mathbf{H}}^{a}$. It is understandable that $\Delta_{\mathbf{X}}^{a}$ would give such

It is understandable that Δ_X^a would give such poor correlation with substituent parameters as H_a , because of its proximity to the trichlorophenyl ring, would be most affected by deviations from an X-independent conformation; small variations would be less significant for H_b and H_c . In addition, d_m and σ_m vary over a smaller range than do the corresponding ortho and para parameters used for the six substituents. Considering the inherent errors in the substituent parameters and the reasonably small variations in the Δ_X^j values, it is satisfying that the correlations for H_b and H_c are as good as they are.

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FIG. 4. Plot of $\Delta_x^a vs. \sigma_m$.

Further evidence in favor of the theory can be obtained from a more explicit consideration of the conformations involved. If each diphenyl ether in series 3 (X \neq H) adopts only the "H_a-inside" conformation⁵ then

[12]
$$\delta_{\omega X}{}^{j} = \lambda_{0}{}^{j}$$

where $\lambda_0{}^j$ is the "other-ring" shielding in that conformation, assuming that the COC bond angle and other parameters do not vary with X. To account for the equivalency of H_a and X, and H_b and H_c when X = H where $\lambda_n{}^j$ is the "other-

[13]
$$\delta_{\omega H}{}^{j} = (\lambda_{0}{}^{j} + \lambda_{\pi}{}^{j})/2$$

ring" shielding for the *j*th proton in the "H_a-outside" conformation (the ring has been rotated through 180°). At this level of approximation

[14]
$$\delta_{\omega \mathbf{x}}{}^{j} - \delta_{\omega \mathbf{H}}{}^{j} = (\lambda_{0}{}^{j} - \lambda_{r}{}^{j})/2$$

Since H_b and H_c would exchange places in a rotation of the X-containing ring through 180°, $\lambda_0^{\ b} = \lambda_\pi^{\ c}$ and $\lambda_\pi^{\ b} = \lambda_0^{\ c}$. Therefore,

[15]
$$\delta_{\omega X}{}^{b} - \delta_{\omega H}{}^{b}$$
$$= (\lambda_{0}{}^{b} - \lambda_{\pi}{}^{b})/2$$
$$= (\lambda_{\pi}{}^{c} - \lambda_{0}{}^{c})/2 = -(\delta_{\omega X}{}^{c} - \delta_{\omega H}{}^{c})$$

⁵Evidence from variable temperature n.m.r. studies (to be presented in a later paper) indicates this assumption is valid.

The experimental data show that the relationship expressed by [15] is observed, as $\delta_{\omega x}{}^c - \delta_{\omega H}{}^c = 0.135 \pm 0.003 \text{ p.p.m.}$ and $\delta_{\omega x}{}^b - \delta_{\omega H}{}^b = -0.140 \pm 0.002 \text{ p.p.m.}$ Thus the model has passed an important test that is independent of any particular theory for the source of the magnetic anisotropy in aromatic rings.

The data obtained for series 3 indicate that the double-difference technique works well and that the assumption that the ether conformation is independent of X is a reasonable one.

Determination of Conformation

The three angular parameters θ , ϕ , and ψ necessary to fix the conformation of a diphenyl ether can be defined as follows: θ is the COC bond angle, ϕ is the angle the ring containing H_a, H_b, and H_c makes with the COC plane, and ψ is the angle the trichlorophenyl ring (the "other-ring") makes with the plane perpendicular to the COC plane but containing the CO bond. Such a definition means that when the molecule is in the "H_a-inside" conformation (Fig. 1), both ϕ and ψ are zero. The signs of ϕ and ψ are set as being positive for counterclockwise rotation when viewed along the respective CO bonds toward the oxygen.

If z_j and ρ_j are the coordinates defining the distance of H_j above the plane of the trichlorophenyl ring and the distance in the plane of the ring from its center, respectively (Fig. 5), then it is a straightforward matter to derive expressions for these coordinates in terms of the three angular parameters.

Although it represents an oversimplification, it is, nonetheless, instructive to see what happens if both ϕ and ψ are set equal to zero ("H_a-inside" conformation). In such a conformation, the shielding at H_a and H_b becomes a maximum. Using the appropriate calculated values of ρ and



FIG. 5. Coordinate system relative to the center of the trichlorophenyl ring of series 3.

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TABLE 2.	"Other-ring" shielding values calculated f	or
	the " H_a -inside" conformation*	

θ	λ_0^a (p.p.m.)	λ_0^b (p.p.m.)	λ ₀ ^c (p.p.m.)
110 115 120 130	-2.722 -2.026 -1.500 -0.811	-0.358 -0.284 -0.222 -0.126	0.038 0.047 0.056 0.067
*φ = 1	$\psi = 0$. See Fig. 1.		

z, and the ring current shielding tables of Johnson and Bovey (4) the "other-ring" shielding shift has been calculated for each ring proton. These values, which are presented in Table 2 for four different θ 's, are the $\lambda_0{}^j$ used in eqs. 12 to 15 (the subscript 0 means that $\phi = 0$). For purposes of obtaining this datum, the CO length, L, was taken to be 1.28 Å, the value found by Toussaint (14) for 4,4'-dibromodiphenyl ether. Tables supplied by Farnum and Wilcox (5) gave similar values for $\lambda_0{}^j$ although they are larger in magnitude by 10 to 20% than those obtained using the tables of Johnson and Bovey.

Since $\delta_{\omega X}{}^j - \delta_{\omega H}{}^j$ would be $(\lambda_0{}^j - \lambda_\pi{}^j)/2$ for the "H_a-inside" conformation (from eq. 14), these have been calculated for the same COC angles and are shown in Table 3.

On the basis of a pure "H_a-inside" conformation, the three calculated values for $\delta_{\omega x}{}^{j} - \delta_{\omega H}{}^{j}$ are not internally consistent for any COC angle, θ , when compared with the experimental ones (-0.396, -0.140, and 0.135 p.p.m.). For example, if the experimental and calculated values for $\delta_{\omega x}{}^{b} - \delta_{\omega H}{}^{b}$ or $\delta_{\omega x}{}^{c} - \delta_{\omega H}{}^{c}$ are matched, θ would have to be in the neighborhood of 120°. At this angle, the calculated $\delta_{\omega x}{}^{a} - \delta_{\omega H}{}^{a}$ is more than twice the experimental -0.396 p.p.m. Common sense suggests that the actual conformation must account for librations in the angles ϕ and ψ even if H_a is "inside". How large these librations should be and how the infinite

TABLE 3. $(\lambda_0 ^{J} - \lambda_n ^{J})/2$ calculated for the "H_a-inside" conformation*

θ	$\frac{(\lambda_0^a - \lambda_n^a)/2}{(p.p.m.)\dagger}$	$(\lambda_0^b - \lambda_\pi^b)/2$ (p.p.m.)	$\begin{array}{c} (\lambda_0{}^c - \lambda_^c)/2\\ (\mathrm{p.p.m.}) \end{array}$
10	-1.454	-0.198	0.198
15	-1.107	-0.165	0.165
20	-0.844	-0.139	0.139
30	-0.500	-0.096	0.096

 $\phi = \psi = 0$. See Fig. 1. $\lambda_{\pi^{\alpha}}$ is approximately 0.190 p.p.m. regardless of the value of θ .

number of conformations generated by them should be averaged to give an average value of $\delta_{\omega X}{}^{j} - \delta_{\omega H}{}^{j}$ is difficult to judge.⁶ However, the use of equations for z and ρ and tables of ring shielding parameters shows that as ϕ and ψ increase from zero, the shielding drops off far more rapidly for H_a than for either H_b or H_c . For example, with $\theta = 120^\circ$, if $\phi = \psi = 15^\circ$, $\delta_{\omega X}{}^{j} - \delta_{\omega H}{}^{j}$ would be -0.46, -0.12, and 0.12 p.p.m. for j = a, b, and c, respectively. This assumes that when X = H, the two "H-inside" conformations with $\phi = 15$ and 165° are still equally probable to account for magnetic equivalence. Thus it is quite reasonable to have $\theta = 120^{\circ}$ and $\delta_{\omega X}{}^{j} - \delta_{\omega H}{}^{j} = -0.40, -0.14,$ and 0.14 p.p.m. provided that ϕ_{av} and ψ_{av} are sufficiently large.7

Although no estimates of the COC bond angle have been made previously for diphenyl ethers as highly substituted as those used in this study, Toussaint (14) estimated the angle in solid 4,4'-dibromodiphenyl ether to be 123° by X-ray studies and Leonard and Sutton (15) obtained a value of 116 \pm 4° for diphenyl ether itself from dipole moment studies. The present work suggests an angle not larger than 120° but probably greater than 115°, surprisingly in good agreement with the literature when one considers the simplicity of the model used.

Besides the previously mentioned simplifications, the ring current picture is itself a classical model and may not adequately give a threedimensional representation of the associated magnetic field. The π -current is undoubtedly more dispersed than the two currents separated by 1.28 Å in the Johnson-Bovey model (the Farnum-Wilcox, double torroidal-shell model predicts a slightly larger value for θ). How substituents such as three chlorines affect the ring current is, of course, unknown but the possibility of the effect being substantial cannot be ruled out.

Finally, although a specific series of diphenyl ethers was studied, any group of diphenyl com-

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⁶Work is presently underway on computer averaging of the possible conformations to obtain better estimates of $\delta_{\omega x}{}^{J} - \delta_{\omega H}{}^{J}$ to compare with the experimental values. ${}^{7}\delta_{\omega x}{}^{a} - \delta_{\omega H}{}^{a}$ can be made equal to -0.40 p.p.m ($\theta = 120^{\circ}$) if the conformation is taken to be 70% pure "H_a-inside" and 30% "H_a-outside". However, $\delta_{\omega x}{}^{b} - \delta_{\omega H}{}^{b}$ would then be -0.05 p.p.m., a value far too low to be acceptable. Also see footnote 5.

pounds could have been used provided that a corresponding group of monophenyls was also available. An extension to benzophenones, diphenylmethanes, and diphenyl sulfides is presently underway.

Experimental

All nuclear magnetic resonance (n.m.r.) data reported were recorded using a Varian A-60-A spectrometer on a scale of 100 Hz sweep width, calibrated by means of a side-band method. All the lines in the aromatic 3- and 4-proton region were reproduced to within ± 0.2 Hz by means of ABC or AA'BB' calculations done by means of the computer. $\Delta_{\mathbf{x}}^{J}$ values were obtained as follows: the aromatic proton chemical shifts were measured on the corrected 100 Hz sweep width relative to a generated side-band of tetramethylsilane as an internal standard (2% v/v) and the four appropriate shifts were used to calculate $\Delta_{\mathbf{x}}^{J}$. Because tetramethylsilane was used as the standard for shift measurements, negative values of $\Delta_{\mathbf{x}}^{j}$ indicate that the *j*th proton was more shielded in the diphenyl ether than in the corresponding anisole. All the compounds were dissolved in chloroform-d at a concentration less than 9 mg/0.5 ml. No concentration effects were noticed provided the concentration was kept below this value. In many cases no concentration effects were noticed at all.

Melting points were determined on a Kofler, micro hot stage apparatus and are reported uncorrected.

The preparation and properties of the following have been described previously (1, 17): methyl 4-methoxy-3nitrobenzoate (2a); methyl 3-amino-4-methoxybenzoate (2b); methyl 3-iodo-4-methoxybenzoate (2c); methyl 4-methoxybenzoate (2d); methyl 3,4-dimethoxybenzoate (2e); 2-(4'-carbomethoxy-2'-nitrophenoxy)-1,3,5-trichlorobenzene (3a); 2-(2'-amino-4'-carbomethoxyphenoxy)-1, 3,5-trichlorobenzene (3b); 2-(4'-carbomethoxy-2'-iodophenoxy) - 1,3,5 - trichlorobenzene (3c); 2 - (4' - carbomethoxyphenoxy)-1,3,5-trichlorobenzene (3d); 2-(4'-carbomethoxy-2'-methoxyphenoxy)-1,3,5-trichlorobenzene (3e).

Methyl 3-Chloro-4-methoxybenzoate (2f)

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3-Chloro-4-hydroxybenzoic acid $(0.5 \text{ g}, \text{m.p. }170-172^\circ)$ was dissolved in 2 N aqueous sodium hydroxide (20 ml) and dimethyl sulfate (5 ml) was added. Additional base was added as needed to maintain a basic solution. The solution was allowed to stand overnight before being acidified with dilute hydrochloric acid to produce 3chloro-4-methoxybenzoic acid (0.48 g), m.p. $114-115^\circ$ (uncorrected). The methylated acid was refluxed for 10 h with methanol (30 ml), methyl iodide (3.0 ml), potassium carbonate (0.6 g), and a little water. Dilution of the solution with water gave the crude product (0.4 g) which was recrystallized from ligroin (b.p. $100-115^\circ$) as long white needles, m.p. $94-95^\circ$ (uncorrected). A literature value of $94-95^\circ$ is reported for this compound (16).

Methyl 3-Cyano-4-methoxybenzoate (2g)

Methyl 3-amino-4-methoxybenzoate (3.6 g) was dissolved in 6 N hydrochloric acid. After the solution had

been cooled to below 5°, sodium nitrite (1.5 g) was added in small amounts with stirring. A solution of cuprous cyanide was prepared as follows: To a solution of copper sulfate (6.25 g) and sodium chloride (1.62 g) in hot water (20 ml), a solution of sodium bisulfite (1.32 g) and sodium hydroxide (1.75 g) in water (10 ml) was added. The precipitated cuprous chloride was filtered, washed well with absolute ethanol and ether, and was suspended in water (20 ml). Sodium cyanide (3.25 g) in water (5 ml) was added and the resulting solution cooled to 5°. Toluene (50 ml) was poured on top of the cuprous chloride solution before the cold diazonium salt solution, previously brought to neutral by the addition of sodium carbonate, was added slowly and with vigorous stirring. An immediate reaction occurred to yield an orange-red coloration. When addition was complete, the mixture was kept in ice for 0.5 h and then was left at room temperature for an additional 12 h. The toluene was evaporated and the dark residue collected (4.3 g). This material was recrystallized twice from ligroin (b.p. 100-115°), was sublimed and the sublimate was recrystallized from ligroin as a slightly yellow product, m.p. 125-126° (uncorrected). The infrared spectrum showed a peak due to CN stretching.

Anal. Calcd. for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.43, 62.75; H, 4.55, 4.53; N, 7.91, 7.63.

2-(4'-Carbomethoxy-2'-chlorophenoxy)-1,3,5trichlorobenzene (3f)

(a) 2-(4'-Carbomethoxy-2'-iodophenoxy)-1,3,5-trichlorobenzene (5.0 g) was refluxed with cuprous chloride (1.0 g, prepared as outlined under preparation of 2g) in dimethylformamide (50 ml) for 12 h. The mixture was poured into an aqueous solution of acidic ferric chloride. Although the viscous oil that formed would not solidify, it was collected by decanting the water solution and was crystallized from hot ethanol (95%) as dark crystals (1.12 g). Two more crystallizations from ethanol (95%) gave white crystals, m.p. 97-99°. An n.m.r. spectrum of this sample showed the presence of a small amount of the iodo starting material. The analytical sample was prepared by crystallizing the material from petroleum ether (b.p. 37-50°), ligroin (b.p. 100-115°), aqueous ethanol and diethyl ether - petroleum ether (1:1), m.p. 97-100° but the iodo impurity could not be removed completely this way.

Anal. Calcd. for $C_{14}H_8O_3Cl_4$: C, 45.94; H, 2.20; Cl, 38.74. Found: C, 44.62, 44.77; H, 2.05, 1.97; Cl, 36.96, 37.28. This analysis indicates about 8–9% of the iodo starting material.

The n.m.r. data reported for this compound were obtained from the analytical sample.

(b) 2- (2'- Amino-4'-carbomethoxyphenoxy)-1,3,5-trichlorobenzene (5.9 g) was dissolved in glacial acetic acid (40 ml). This solution was added slowly to a second solution of sodium nitrite (1.38 g) in sulfuric acid (20 ml) with the temperature kept below 35° . After 2 h the mixture was added to a solution of cuprous chloride (8.0 g, prepared as outlined under preparation of 2g) in hydrochloric acid (10 ml). Frothing occurred initially but after 2 h the reaction subsided. Dilution with water produced a gummy residue which was dissolved in hot ethanol and filtered, and the filtrate cooled to produce an oil. The oil could be crystallized from methanol only with much difficulty. Two further crystallizations from methanol yielded yellowish crystals, m.p. 96-99°. The infrared spectrum was essentially identical to that of the product produced by method (a) although there were traces of some impurity. The yield by this method was so low as to make it impractical to use it as a preparative procedure.

2-(4'-Carbomethoxy-2'-cyanophenoxy)-1,3,5-

trichlorobenzene (3g)

2-(4'-Carbomethoxy-2'-iodophenoxy)-1,3,5-trichlorobenzene (5.0 g) was refluxed for 4 h with cuprous cyanide (1.11 g) in dimethylformamide (50 ml). The mixture was poured into a solution of ferric chloride (6.0 g) in dilute hydrochloric acid (50 ml). A gum was formed initially but this soon solidified. One recrystallization from ethanol (95%) gave long brown prisms (2.4 g), m.p. 126-128° (uncorrected), whose infrared spectrum showed absorption due to CN stretching. A further recrystallization from ethanol gave the analytical sample, m.p. 129-130° (uncorrected).

Anal. Calcd. for $C_{15}H_8O_3NCl_3$: C, 50.50; H, 2.26; N, 3.93; Cl, 29.84. Found: C, 50.69, 50.93; H, 2.10, 2.15; N, 3.93, 4.32; Cl, 29.39, 29.52.

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