ORDER PARAMETERS AND CONFORMATION OF NEMATIC \( p \)-METHOXYBENZYLIDENE-
\( p \)-n-BUTYLANILINE (MBBA) BY NMR STUDIES OF SOME SPECIFICALLY
DEUTERATED DERIVATIVES

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INTRODUCTION

It is known that nematic liquids have a well defined degree of
order.\(^1\) The order parameter, \( S \), which describes the fluctuation
of the molecular axis from the direction of preferential orientation
of the molecule, is given by

\[
S = \frac{1}{2} (3\cos^2 \xi - 1)
\]

(1)

where \( \xi \) is the angle between the long axis of the molecule and the
direction of its preferential orientation in the nematic phase.

For complete order, \( \cos^2 \xi = 1 \) and \( S=1 \) as in the case of a
crystal, whereas for complete disorder, \( \cos^2 \xi = 1/3 \) and \( S=0 \),
representing an isotropic liquid. Thus the order parameter of a
nematic will lie between 0 and 1 in a fluid. When a molecule is
aligned in a magnetic field, \( H_o \), each nuclear magnetic dipole will
produce an additional field at neighboring nuclei, the component
of which along the direction of \( H_o \) together with \( H_o \) will result
in a total effective field\(^2\)

\[
H_{\text{eff}} = H_o \pm \alpha (3\cos^2 \theta - 1)
\]

(2)

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where $\alpha$ is an interaction field parameter and $\theta$ is the angle between $H_0$ and the line joining the two interacting nuclei.

Equation (2) predicts a pair of resonance lines symmetrically disposed about the field value at which a single resonance line would occur in the absence of the additional field due to the neighboring nuclei. The separation, $\delta H$, of this doublet is thus

$$\delta H = 2 \left| H_{\text{eff}} - H_0 \right| = 2\alpha(3\cos^2 \theta - 1) \quad (3)$$

For proton dipole-dipole interaction, $\alpha = 3/2 \mu_H r^{-3}$, where $\mu_H$ is the proton nuclear moment ($1.42 \times 10^{-23}$ erg/gauss) and $r$ is the distance between the two interacting protons. Thus, from equation (3), the separation of the doublet as a result of the magnetic dipole-dipole interaction of a pair of protons $H_j$ and $H_k$ held in a rigid orientation is

$$\delta H_{jk} = 3 \mu_H r^{-3}_{jk} (3\cos^2 \Theta_{jk} - 1) \quad (4)$$

Molecules of a nematic liquid in a magnetic field of a few thousand gauss are aligned with their long axes approximately parallel to the field. The angular-dependence term in equation (4) for a nematic liquid should be replaced by a mean value for the motions involved. Therefore,

$$\delta H_{jk} = 3 \mu_H r^{-3}_{jk} <3\cos^2 \Theta_{jk} - 1> \quad (5)$$

This angular-dependence term can be evaluated by considering all possible ordering factors in the molecule with reference to the direction of the applied magnetic field.

Consider a molecule of MBBA-$d_{17}$ lying arbitrarily with its long axis $OL$ making an angle $\zeta$ with the preferred axis $OP$ in a magnetic field $H_0$, as represented in Figure 1. The thermodynamic average term can be represented by a number of orientation terms:

$$<3\cos^2 \Theta_{jk} - 1> = (3/2 \cos^2 \gamma - 1/2) (3/2 \cos^2 \phi - 1/2) \quad (6)$$

$$\times (3/2 \cos^2 \xi - 1/2) (3 \cos^2 \Theta_o - 1)$$

where $\Theta_o$ is the angle between the applied magnetic field and the preferred orientation of the molecule, $\gamma$ is the angle between the