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The configuration of dichlorodiphenylethers

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THE CONFIGURATION OF DICHLORODIPHENYLETERS

by

Wayne Lavelle Brantley


UC 1968

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

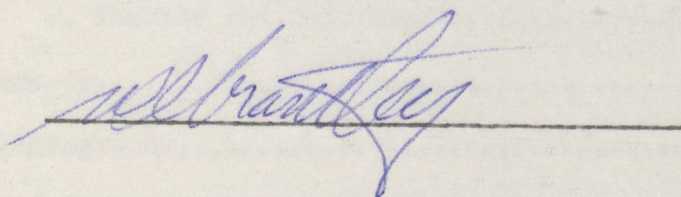
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This Thesis

Submitted by

A handwritten signature in blue ink, appearing to read "J. Brantley", is written over a horizontal line.

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a major in Chemistry

is approved by

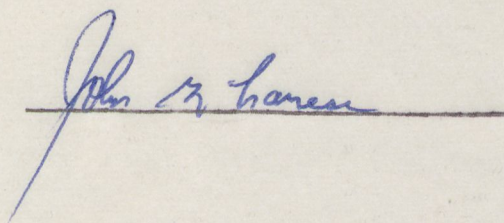
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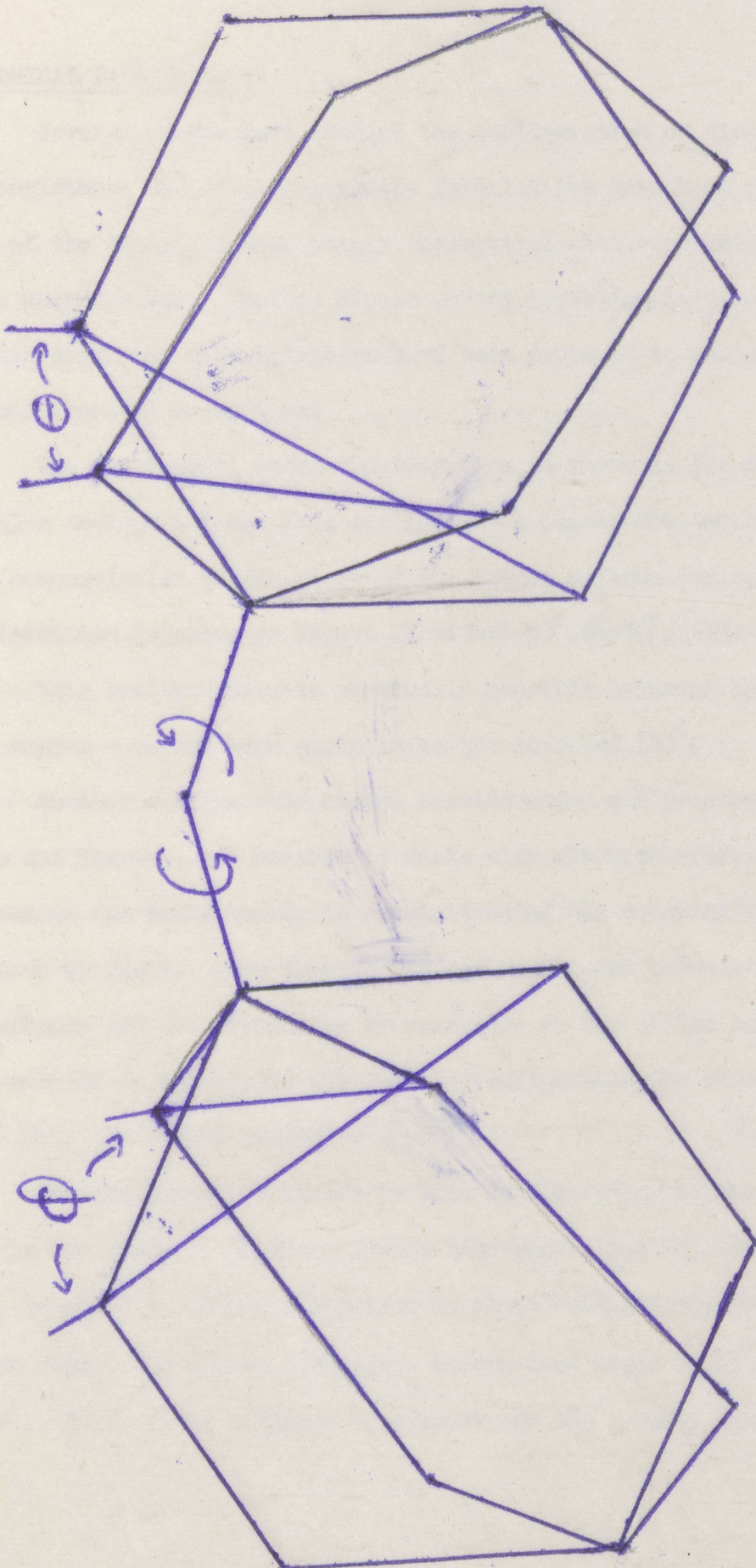
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INTRODUCTION :

No definite molecular configuration of diphenylethers has ever been substantiated by experimental proof.

Due to the free rotation of the benzene rings about the oxygen linkage, the diphenylether can take any number of spatial configurations. Some theoretical work has been done in trying to determine the molecular structure, but it was felt that careful examination of the high resolution nuclear magnetic resonance spectra of the ethers would be useful in determining a structure. (Figure I)

Figure I



HISTORICAL BACKGROUND :

Several groups have studied the configuration of dimethyldiphenylethers and several possible formulations have been proposed. Much of the study has been purely theoretical with supplementary dipole moment study. Besides dipole moment investigations, possible configurations of diphenylethers have been proposed to explain certain chemical mechanisms.

The first model under consideration is known as the Smyth and Walls configuration. This configuration places the two benzene rings perpendicular to the plane of the oxygen valence angle. This configuration is shown in Figure II with $\theta = 90^\circ$, $\phi = 90^\circ$. (1)

This configuration is physically possible assuming the carbon - oxygen - carbon bond angle to be the accepted 120° .

Another configuration under consideration was proposed by Sutton and Hampson, but because it deals with electron orbitals, it is known as the Pauli model, in recognition of the electron orbital work done by Pauli. With this configuration the two benzene rings are coplanar and are stabilized by resonance by way of the lone - pair orbital in the oxygen atom. This configuration is shown in Figure III. With this shape $\theta = 0^\circ$, $\phi = 0^\circ$.

One discrepancy realized in this configuration is the deviation in the carbon - oxygen - carbon bond angle from the accepted 120° . In order to form the required in plane configuration of the benzene rings, the carbon - oxygen - carbon bond angle would have to be 180° . There is no evidence to support the 180° angle, therefore

acceptance of the Pauli model is restricted. (1)

Y. Morino, L. Higasi, and T. Uyev proposed the third model under consideration. In this model the two benzene rings are placed at non-equivalent positions. One ring is placed in the plane of the oxygen valance angle and the other is placed perpendicular to the plane. (Figure IV) In this model $\theta = 90^\circ$, $\phi = 0^\circ$. This model is consistent with the 120° carbon - oxygen - carbon angle. (1)

The three preceeding models have been the most widely accepted of the theorectically proposed molecular structure of diphenylethers.

A great deal of nuclear magnetic resonance work on the configuration of dimethyldiphenylethers has been done by H. Shimizu, S. Fujiwara, and Y. Morino at the University of Tokyo. (2) They have attempted to identify certain characteristic splittings found in the spectra of dimethyldiphenylethers with nonequivalent protons in the benzene ring. They found that liquid di-*o*-tolyl ether existed in a stable asymmetric skewed conformation having nonequivalent methyl groups. The doublet methyl group spectrum had a peak separation of 1.35 cps, at 56.4 Mc/sec.

This work was later refuted in this country by a group led by G.V.D. Tiers of Minnesota Mining and Manufacturing Co. (3) Tiers contended that the splitting was due to methyl protons of co-existing isomers. It is not important to this paper whether the point made by the Japanese group is valid, but the procedure they

used to prove their theory is also used in this work. The Japanese group ran spectra of what may be called the monomer of a dimethyldiphenylether, that is a cresol. By examining the results of the cresol studies they made a comparison with the spectra of the ether. Since the cresol can not possibly have a rotational isomer, since it has no point of rotation, the nuclear magnetic resonance spectrum of the cresol would show no splitting due to a rotational isomer.

Therefore any splitting found in the ether also found in the cresol can not be attributed to the rotation that the ether can undergo. With this logic the Japanese group correlated the splitting not to rotational isomers, but to nonequivalent protons in the benzene ring.

This is a stable theoretical base to start the nuclear magnetic resonance investigation of the spatial configuration of diphenylethers.

FIGURE II - SMYTH and WALLS MODEL

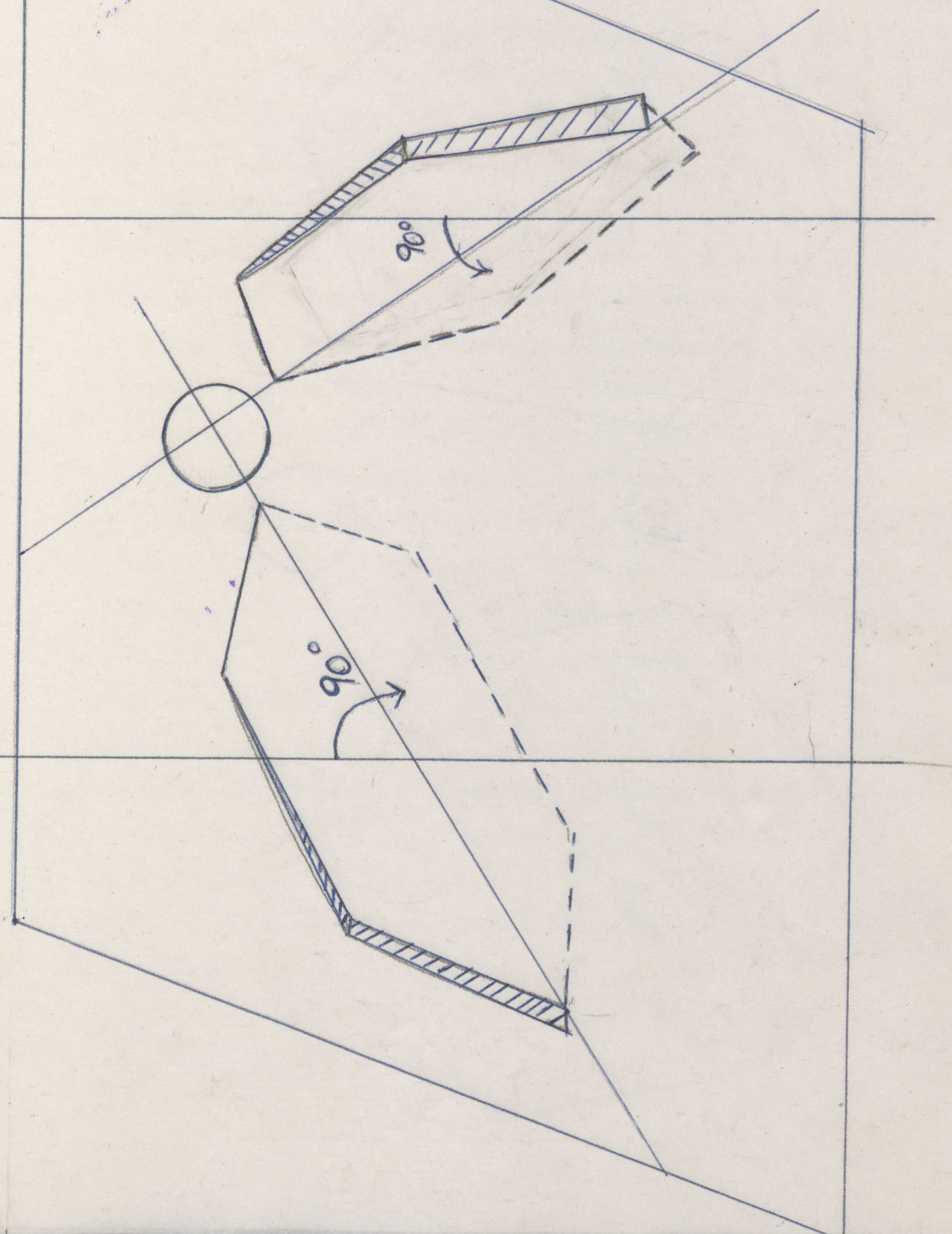


FIGURE III - PAULI MODEL

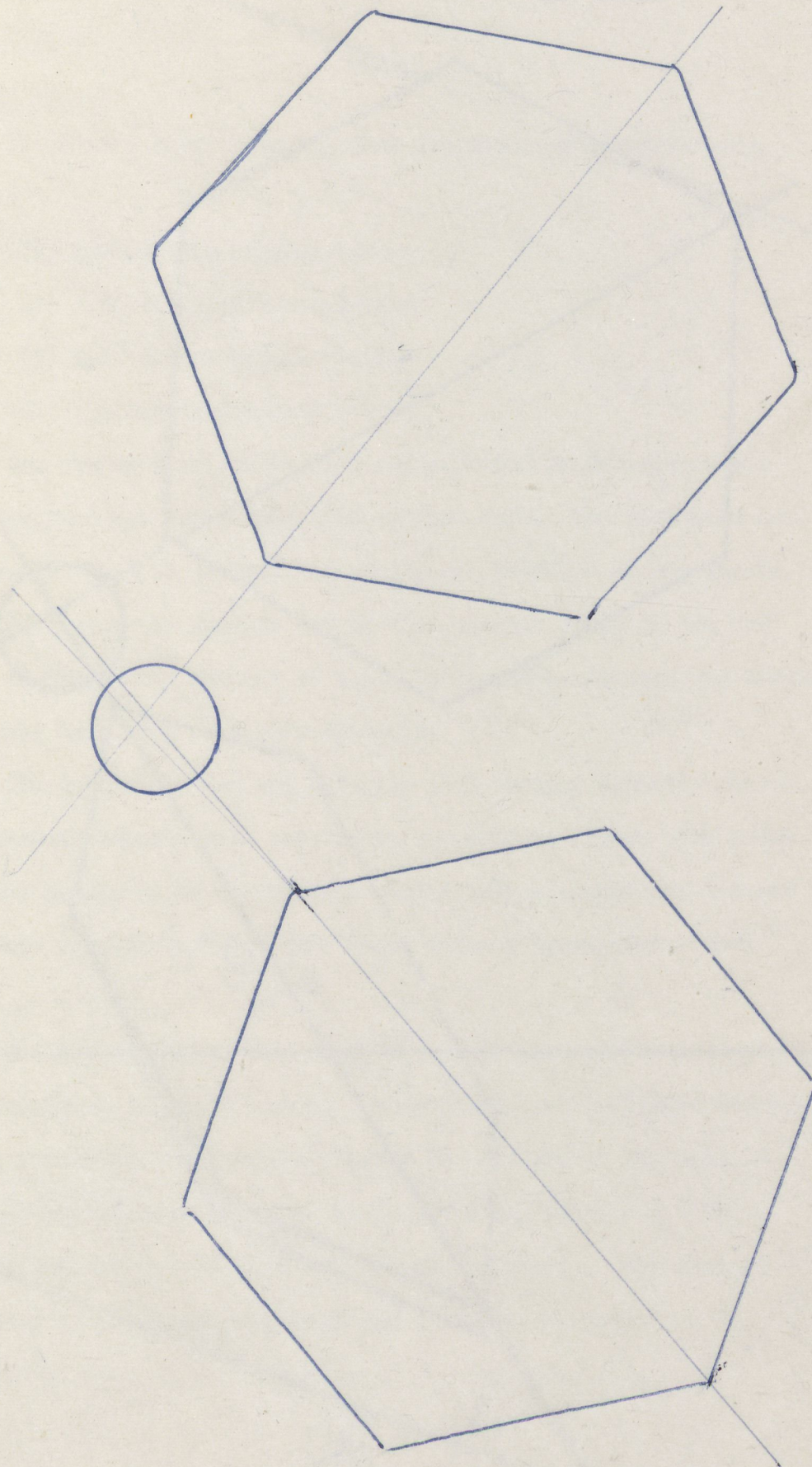
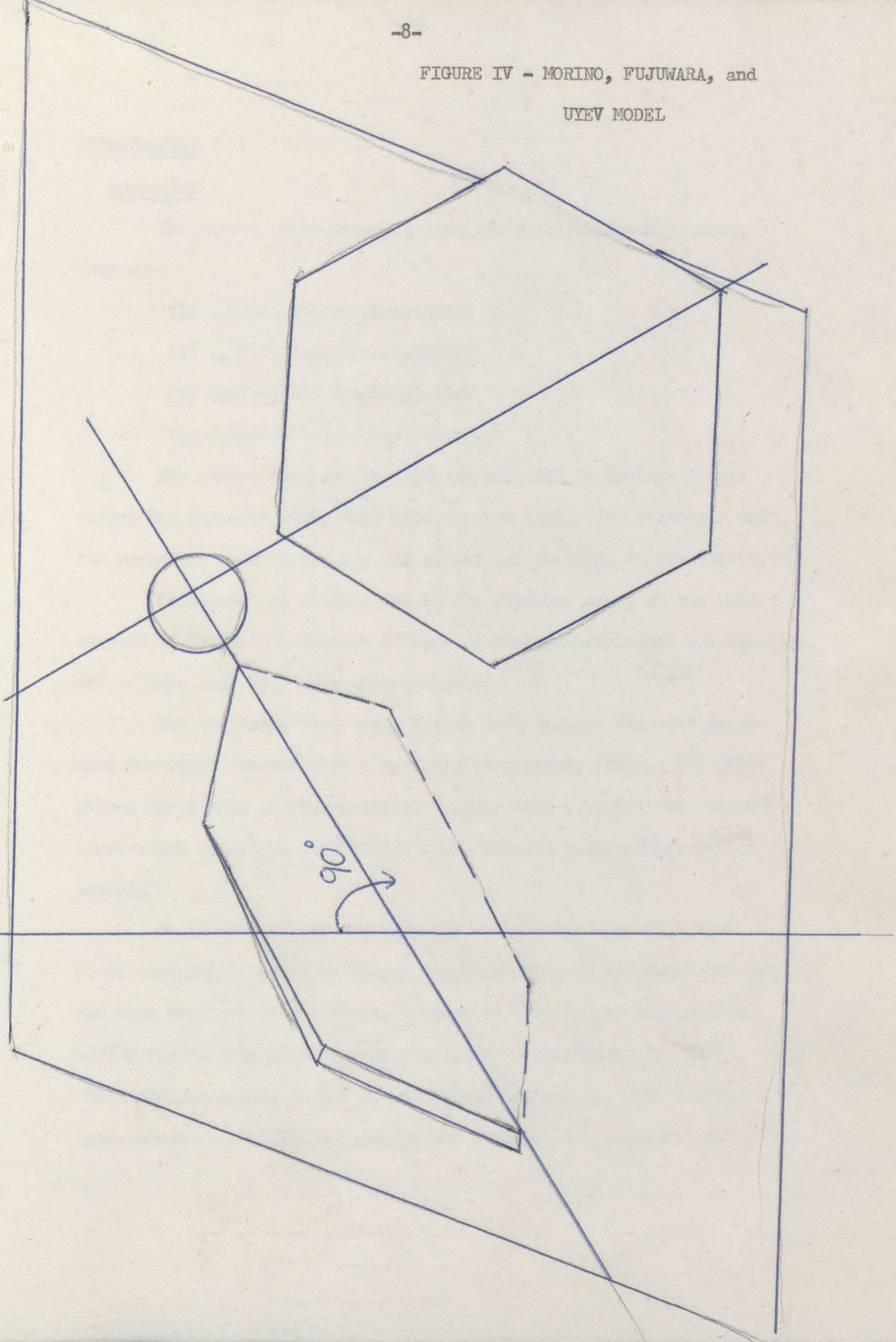


FIGURE IV - MORINO, FUJUWARA, and
UYEV MODEL



EXPERIMENTAL :

Apparatus

The ethers under investigation are dichlorodiphenylethers.

They are:

- (1) 2,2'-dichlorodiphenylether
- (2) 3,3'-dichlorodiphenylether
- (3) 4,4'-dichlorodiphenylether
- (4) 3,4-dichlorodiphenylether

The ethers were synthesized and purified by Dominic Poccia during his research work, June 1966 to June 1967. The synthesis and the procedure used to justify the purity can be found in his thesis.(4)

Following the example set by the Japanese group at the University of Tokyo, the monomer of each dichlorodiphenylether was studied, and in this case they were chlorophenols.

The apparatus used was a Varian A-60 Nuclear Magnetic Resonance Spectrophotometer with a variable temperature probe. The probe allows the sample to be investigated under both elevated and reduced temperature conditions. For this work, reduced temperatures were needed.

On the outside of the magnet's console was mounted a dewer flask containing liquid nitrogen. Gaseous nitrogen is pumped through and into the area of the probe. (Figure V) The liquid nitrogen is -197°C and the gas exiting from the flask is approximately -100°C .

This chilled gas is pumped up and around the sample. The desired temperature is selected beforehand and a thermister contained in

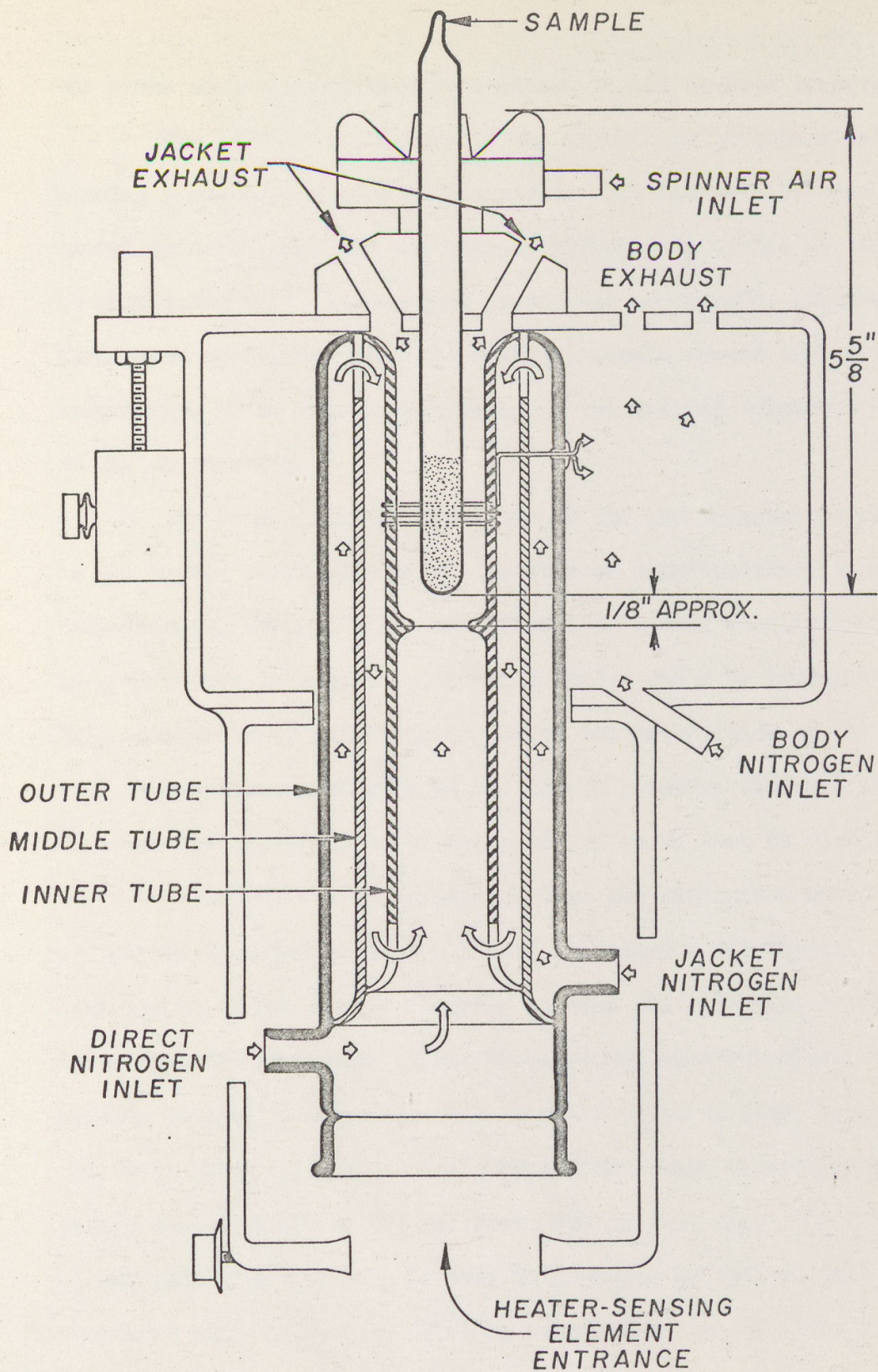


FIGURE V.

Figure 10. Schematic Representation of the V-6031 Probe (5)

the probe controls the heater to adjust to the desired temperature.

The actual temperature of the sample can be determined by placing a methanol sample in the probe. The distance between the methyl hydrogen peak and the hydroxy hydrogen in cycles per second is correlated with temperatures in degrees centigrade. (Figure VI) Continuous monitoring with the methanol sample showed the actual temperature to be within one degree of the desired temperature preset on the thermostat.

The reason for the necessity of the low temperature probe is due to the complexity of the spectra of diphenylethers at room temperatures. (Figure VII) Any attempt to assign certain hydrogens in a structure to a certain chemical shifts would be impossible. This complexity of splitting is due to the interaction of the multitude of hydrogens available in the freely rotating diphenylethers. In order for any study to be made, the spectra must be simplified. The most convenient way to accomplish this simplification would be to reduce the interaction of the nuclei by reducing the motion. The best way to remove energy in order to slow the molecular rotation is to cool the compound. Since these ethers have relatively high melting points, cooling the neat compound would be very unsatisfactory for there would be a very small temperature range between a sufficiently slowed compound and the formation of crystals. The formation of any number of crystals is very intolerable in nuclear magnetic resonance work because of the long relaxation time of these solids.

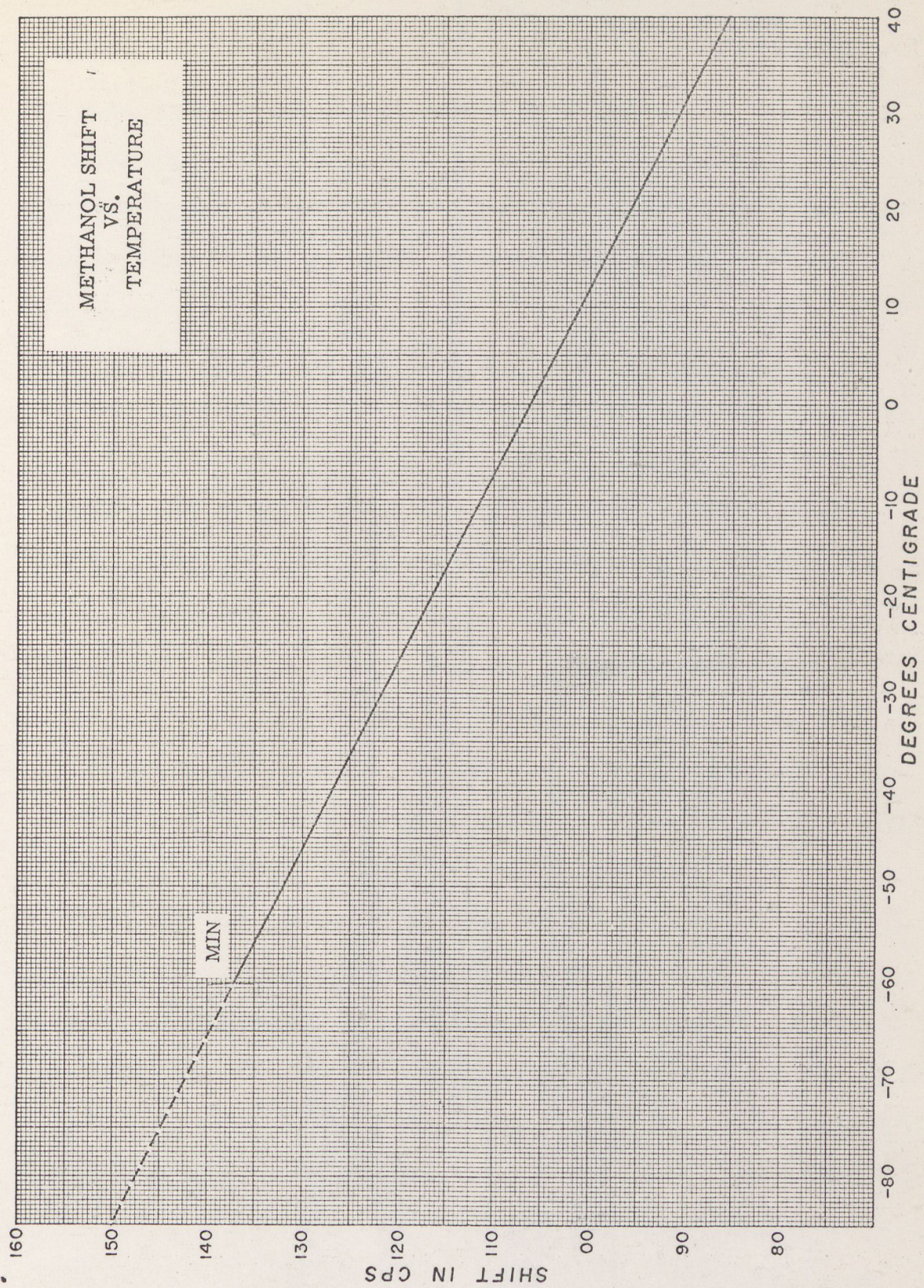
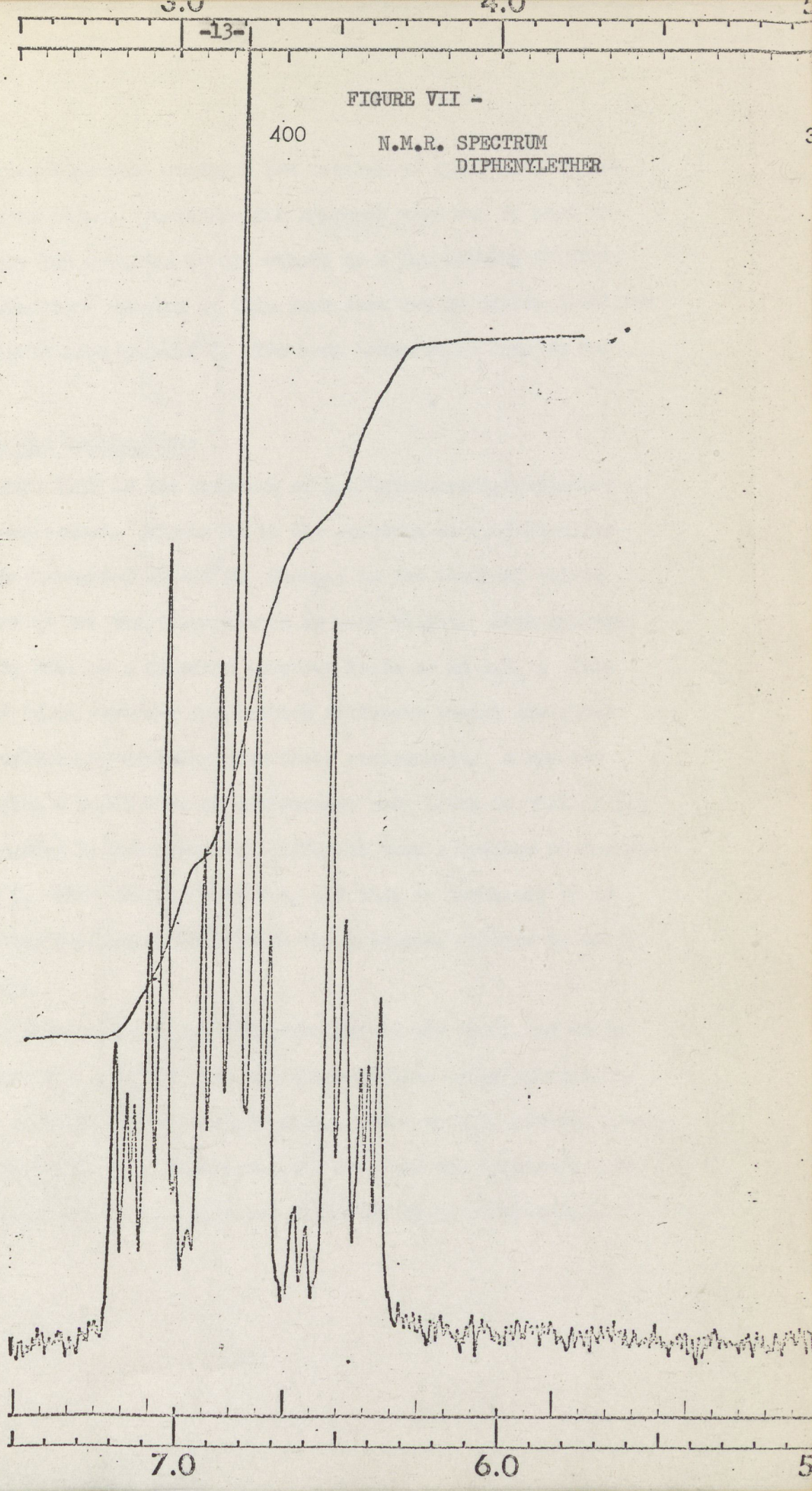


Figure 22:VI Methanol Shift vs. Temperature (5)

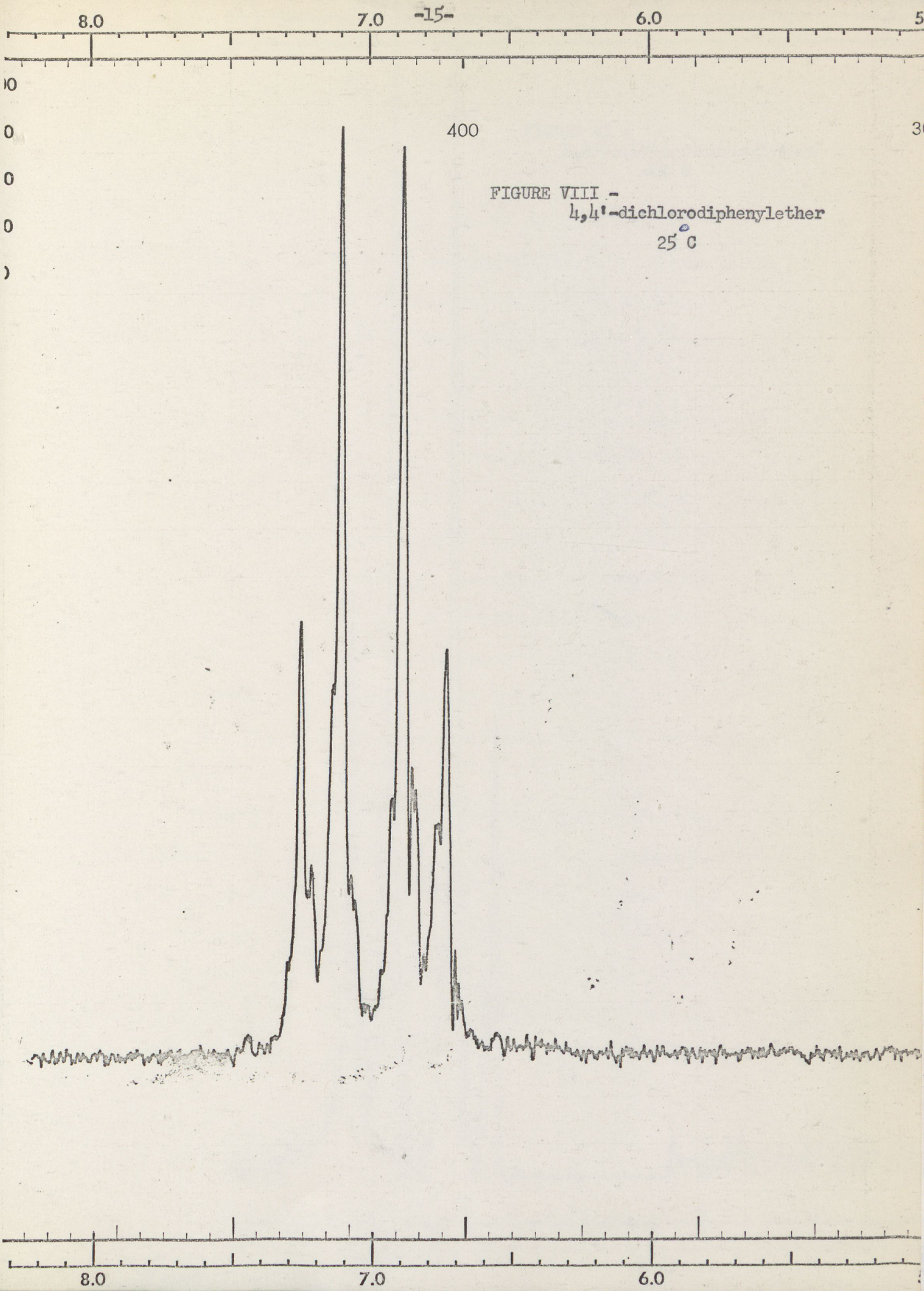


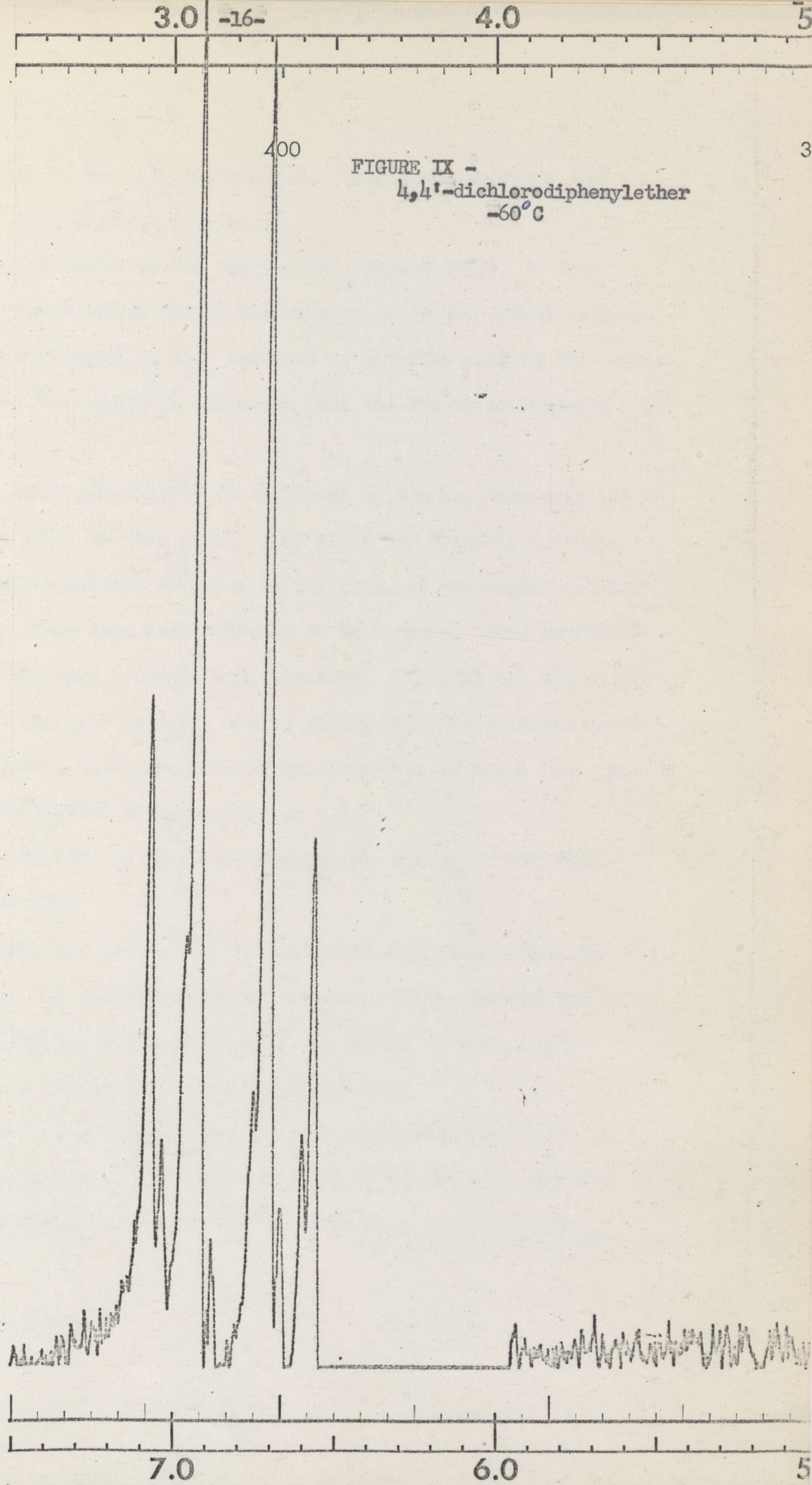
The long relaxation time produces low resolution spectra which are of no analytic value. Therefore the approach used was to cool an approximately 10% solution of the ethers in a low melting solvent. The low temperature spectra in this work were run in carbon disulfide which is liquid down to -112°C . The room temperature spectra were run neat.

Results and Conclusions:

Figure VIII is the spectrum of 4,4'-dichlorodiphenylether at room temperature. Figure IX is the spectrum of 4,4'-dichlorodiphenylether obtained at -60°C . Changes in the chemical shifts of the ether at the two temperatures is very slight. Both spectra conform very well to a standard spectrum known as an A_2B_2 . This designation is an arbitrary one in which different nuclei are given letter designations depending upon their environment. A nucleus of designation A would have an environment very close to that of one with designation B, but much more different than a nucleus of designation X or Z. With this information, all that is necessary is to find the ether configuration in which the hydrogens conform to an A_2B_2 pattern.

The first configuration to consider is the Symth and Walls model (Figure II). In this the two chlorobenzene rings are perpendicular to the plane of the oxygen atom.. Here an A_2B_2 pattern exists with the hydrogens near the oxygen, the A's, and the hydrogens next to the chlorines the B's. Only two different types of hydrogens





and ^{they} conforming to the A_2B_2 designation. Therefore the Smyth and Walls model is a distinct possibility.

The next model is the Pauli model (Figure III). In this model, the benzene rings lie in the same plane as the oxygen valance bond. With this model an A_2B_2 spectrum is possible only if the carbon-oxygen-carbon bond angle is different than the 120° it is believed to be.

The third possibility is the model of Morino, Fujiwara, and Uyev (Figure IV). In this model, they place the rings in nonequivalent positions in which one lies in the plane of the oxygen valance bond and the other lies perpendicular to this plane. This configuration would not give a simple A_2B_2 spectrum. Although the out of the plane ring would give an A_2B_2 , the in plane, with its shielded hydrogen, would give a much more complex spectrum with at least four additional nonequivalent hydrogens than an A_2B_2 .

The evidence in this case would favor the Smyth and Walls model (Figure II).

Figure X is the monomer of 4,4'-dichlorodiphenylether, p-chlorophenol. As would be expected, because of the symmetry and the lack of interaction of the chlorines, the phenol is very similar to the ether and displays the same A_2B_2 pattern.

Figure XI is the spectrum of 3,3'-dichlorodiphenylether at room temperature and Figure XII is a spectrum of the same compound diluted in carbon disulfide at -60°C . With this pair of spectra,

2.0

3.0 -18-

4.0

5.0

30
20
10
0

400

FIGURE X -

p-chlorophenol

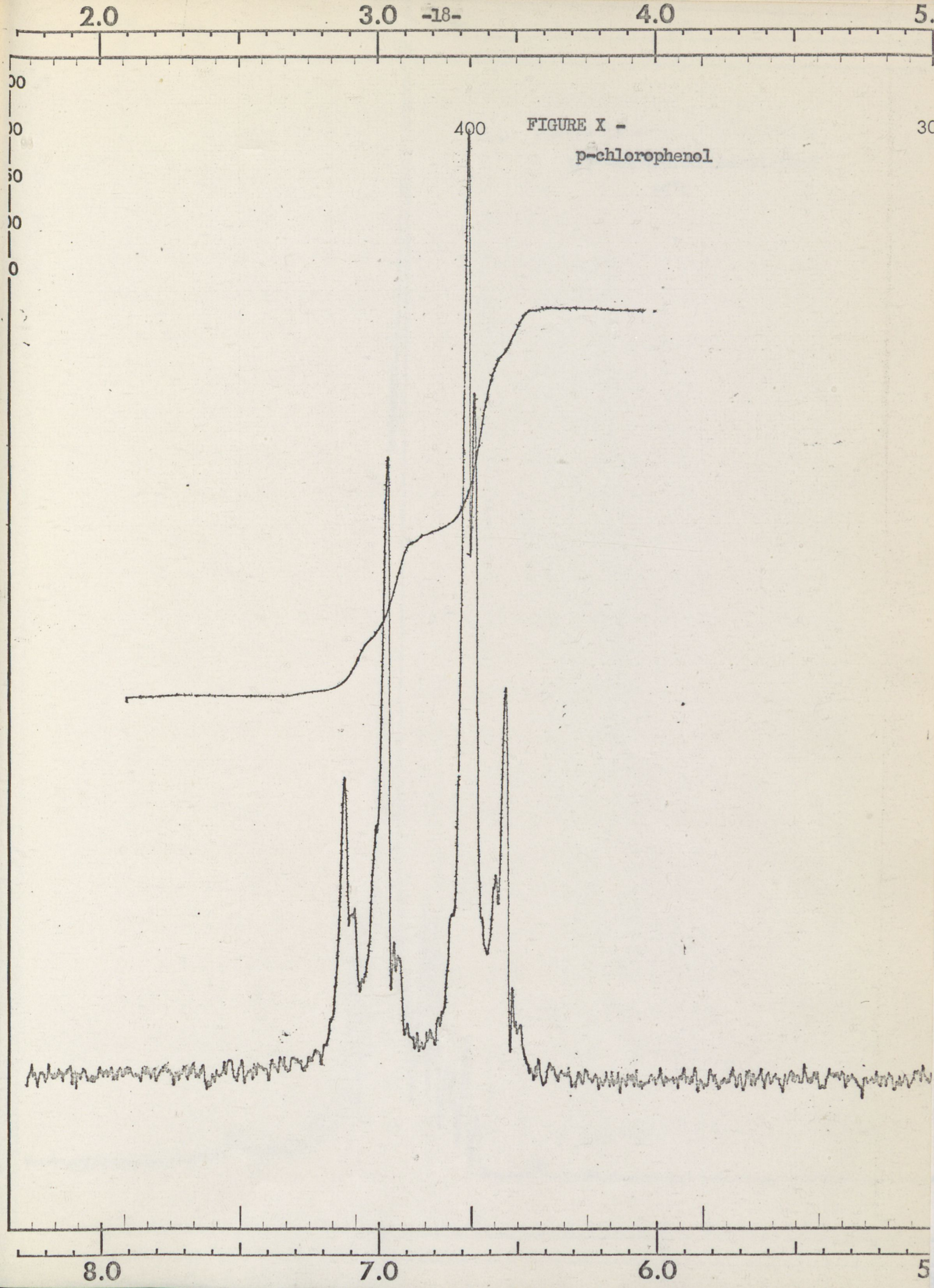
30

8.0

7.0

6.0

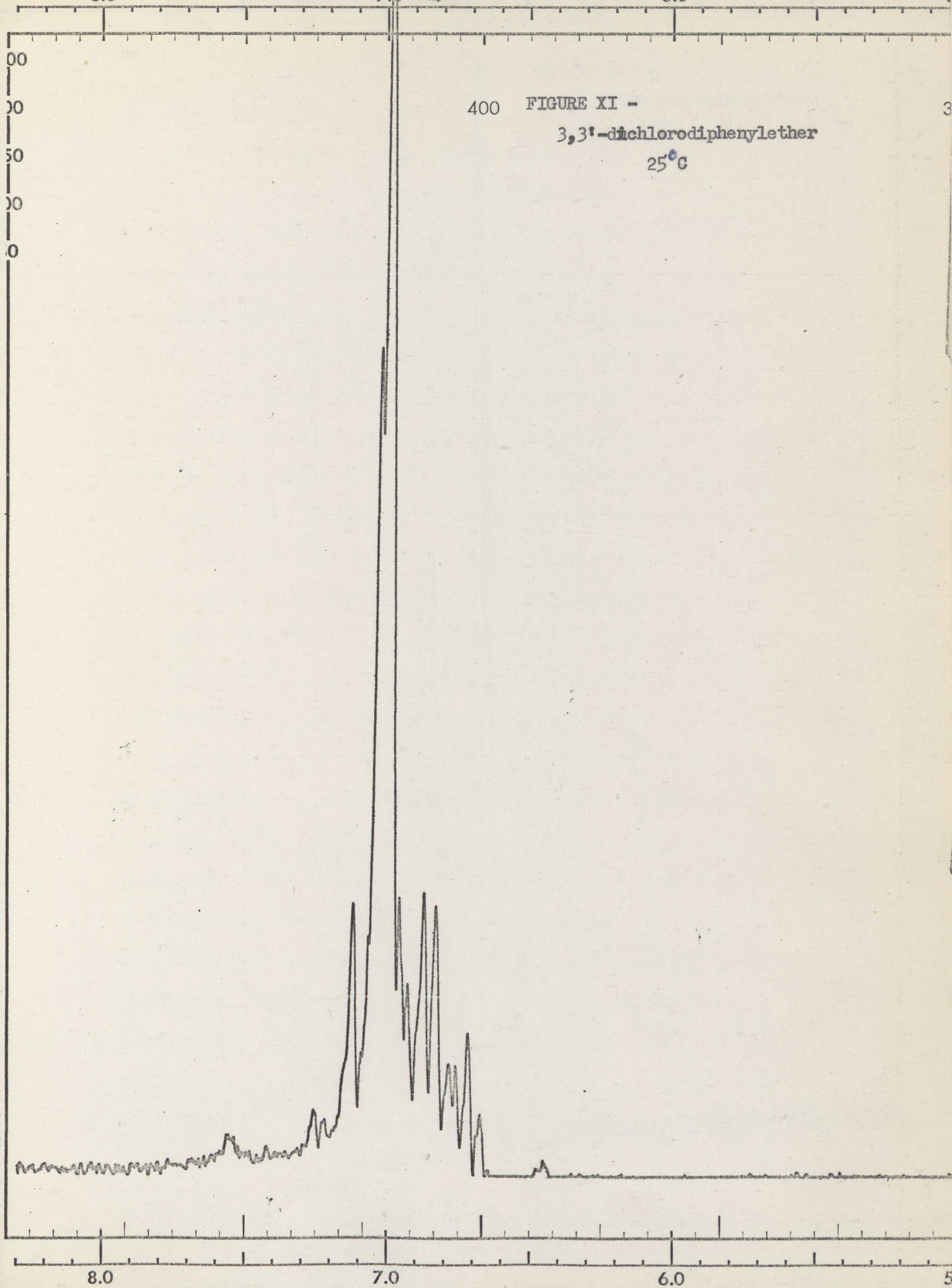
5.0



8.0

7.0 -19-

6.0



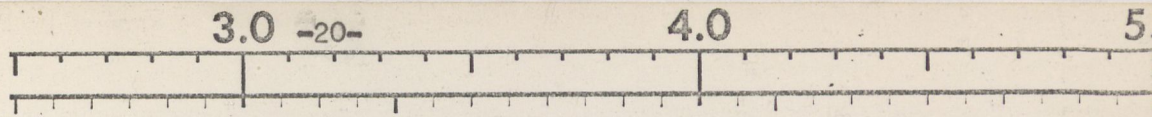
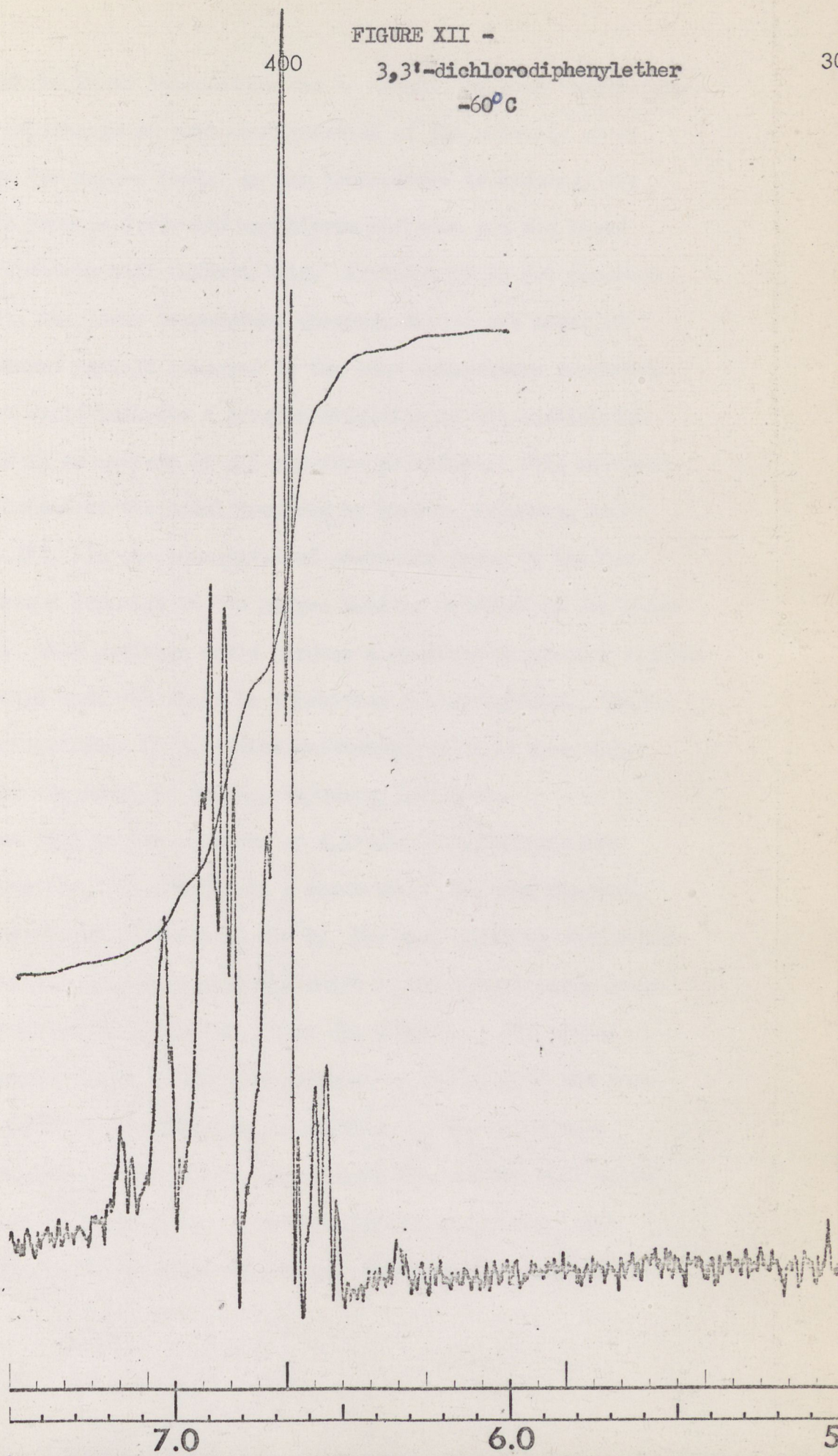


FIGURE XII -

3,3'-dichlorodiphenylether

-60°C



the effect of the lower temperature can be noted. The room temperature spectrum is an average of each configuration of the molecule as it rotates about the oxygen bond. As the temperature is reduced, the molecule will tend to favor its equilibrium position and the lower temperature spectrum will reflect this. Although it is not apparent in Figure XII, the lower temperature chemical shifts are moved 20 cycles per second upfield compared to the room temperature spectrum. This movement would indicate a greater shielding in the equilibrium position than in an average of all possible positions. This movement could be explained by the model proposed by Morino, Fujuwara, and Uyev (Figure IV). In the nonequivalent positions taken by the two rings, a hydrogen adjacent to the oxygen bond is shielded by the other benzene ring. This position would produce a spectrum of greater shielding than a model with the rings in a position of equivalence. Therefore, the configuration of 3,3'-dichlorodiphenylether is favorably represented by the model of Morino, Fujuwara, and Uyev.

Figure XIII is the spectrum of 2,2'-dichlorodiphenylether at room temperature. Figure XIV is a spectrum of the same compound in a carbon disulfide solution at -60°C . The most striking difference to be noted in the two spectra is the shift of the center peaks within the two outer chemical shifts. This was a shift of six cycles per second toward a more deshielded position in relation to the room temperature spectrum. Deshielding in relation to the difference between the average spin spectrum and a lower temperature equilibrium would tend to refute the model of Morino, Fujuwara, and Uyev with its aspect of greater nuclear shielding. This model proposed by the

8.0

7.0

-22-

6.0

5

00
00
50
00
0

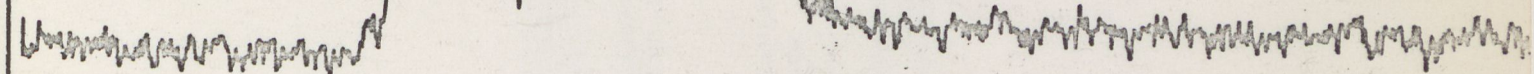
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FIGURE XIII -

2,2'-dichlorodiphenylether

25°C

30

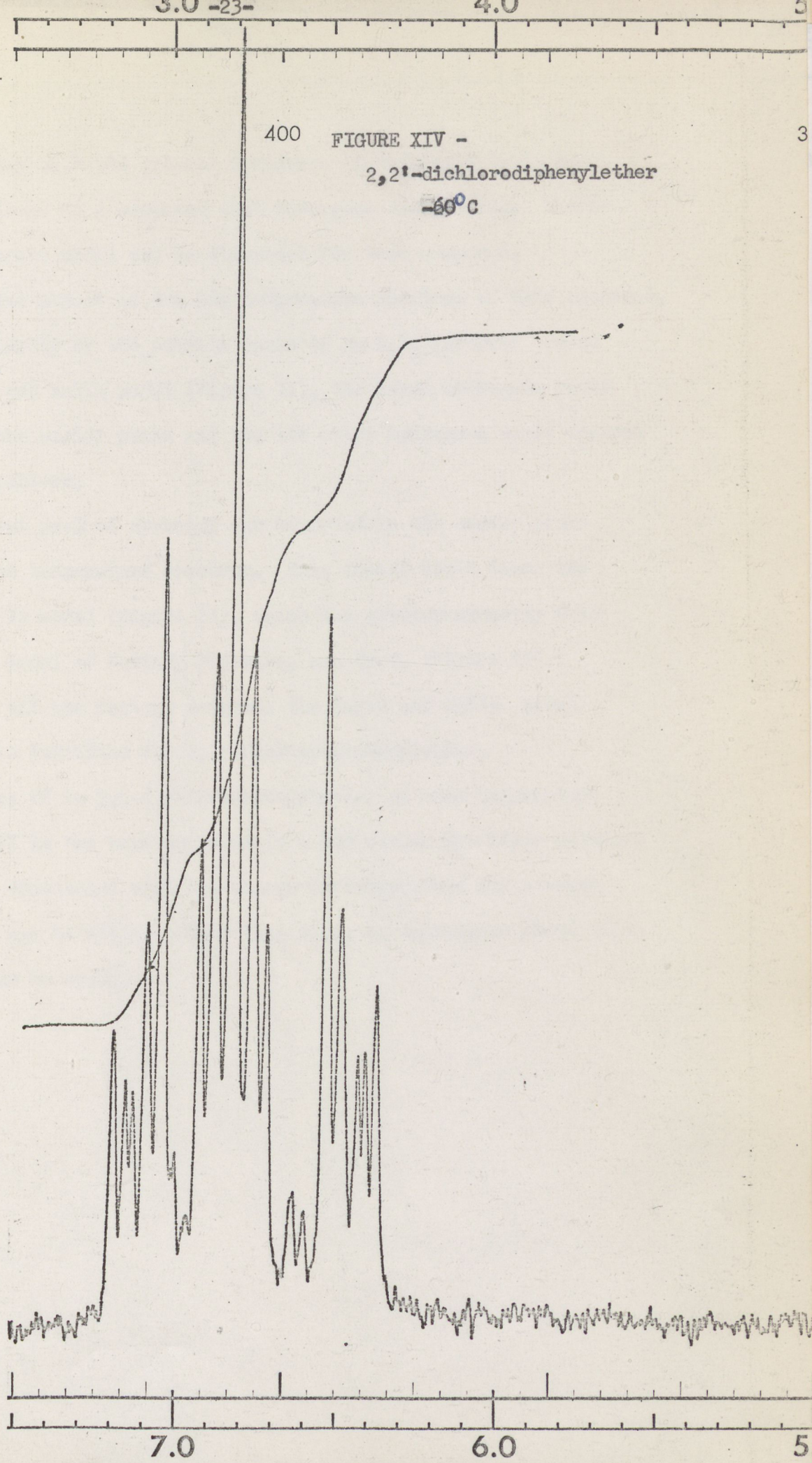


8.0

7.0

6.0

5



Japanese group with its greater incidence of shielding would contribute the least to a compound that undergoes deshielding. Therefore the Japanese model can be discarded for this compound.

Another aspect of the low temperature spectrum of this compound, is the similarity of the outside peaks to an A_2B_2 pattern. Going to the Smyth and Walls model (Figure II), the inner hydrogens could account for the center peaks and the two outer hydrogens would account for an A_2B_2 pattern.

A great deal of symmetry can be noted in the center peaks of the reduced temperature spectrum. This aspect would favor the Smyth and Walls model (Figure II), which has greater symmetry than the Japanese model of Morino, Fujiwara, and Uyev. (Figure IV)

With all the factors weighed, the Smyth and Walls model (Figure II) is justified for 2,2'-dichlorodiphenylether.

Figure XV is 3,4-dichlorodiphenylether at room temperature and Figure XVI is the same compound in a 10% carbon disulfide solution at -60°C . A difference with the change in temperature and a vague A_2B_2 pattern can be noted. Other than this, no conclusion about this compound could be drawn.

8.0

7.0

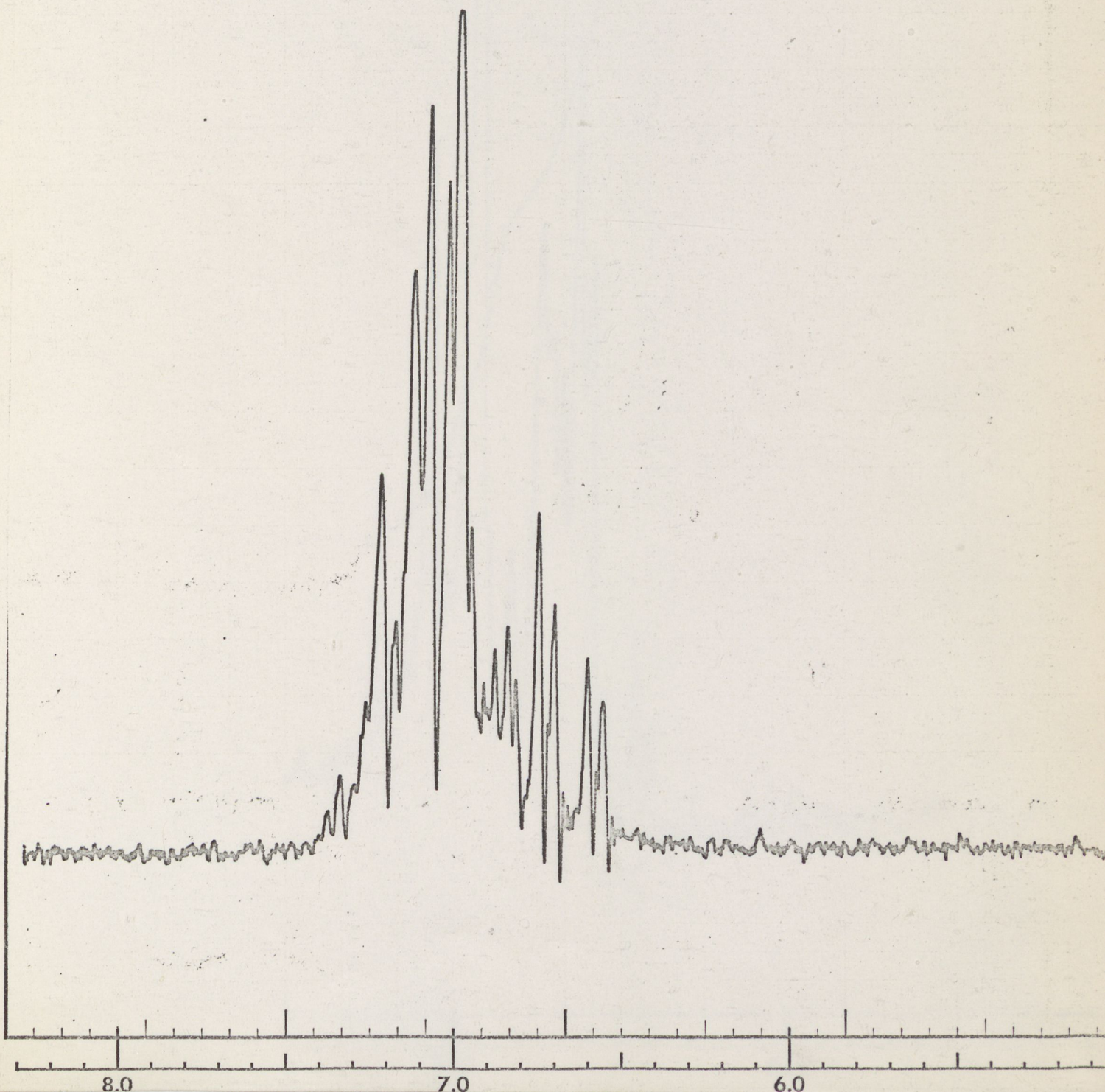
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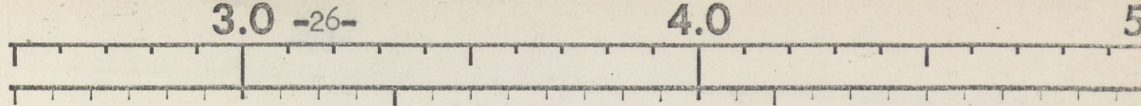
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FIGURE XV *

3,4-dichlorodiphenylether

25°C



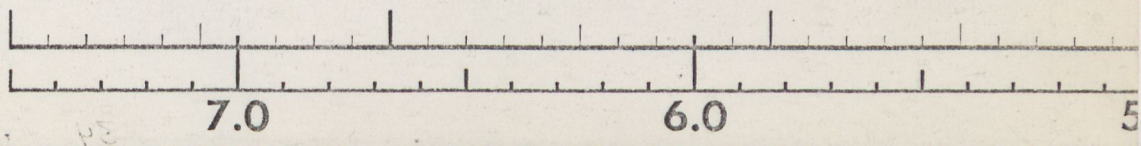
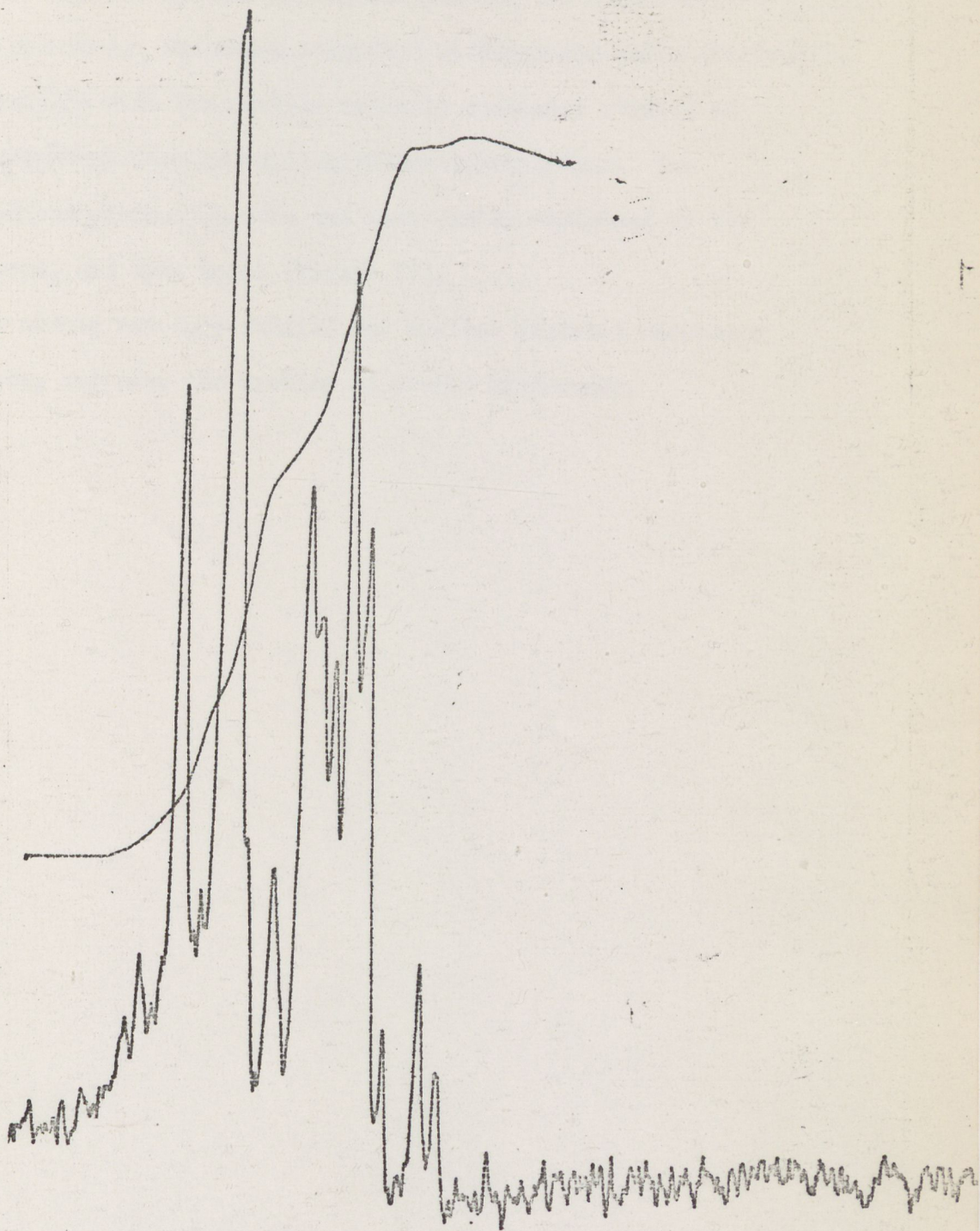


400

FIGURE XVI -

3,4-dichlorodiphenylether

-60°C



SUMMARY:

Low temperature nuclear magnetic resonance has been used in this work to propose spatial configurations for the dichlorodiphenylethers examined. The model suggested by Smyth and Walls (Figure II), is found compatible with the nuclear magnetic resonance studies of 4,4'-dichlorodiphenylether and 2,2'-dichlorodiphenylether. The 3,3' dichlorodiphenylether spectra was most easily explained by the Morino, Fujiwara, and Uyev model (Figure IV).

These models not only fulfill the nuclear magnetic resonance spectra aspects, not also the problem of steric hindrance.

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