DETERMINATION OF RING ORIENTATION IN DIPHENYLMETHANE AND DERIVATIVES

by

Patrick M.ichael Comi III UC 1970

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Submitted by

Patrick M. Comi

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is approved by

John Carnes

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TABLE OF CONTENTS:

Nuclear Magnetic Resonance Spectrometry, like infrared, visible, and ultraviolet spectrometry is a form of absorption spectrometry. Certain nuclei can absorb electromagnetic radiation in the radiofrequency range. These nuclei are able to absorb this energy because they "spin" about their center axis generating a dipole along it. Protons are among those nuclei that absorb radiofrequency energies. If a proton is placed in a magnetic field its dipole can be in one of two possible orientations. It can be in a low energy state aligned with the field, or a high energy state aligned against the field. In its low energy state, a spinning proton will precess about an axis at a particular frequency. (Figure 1).

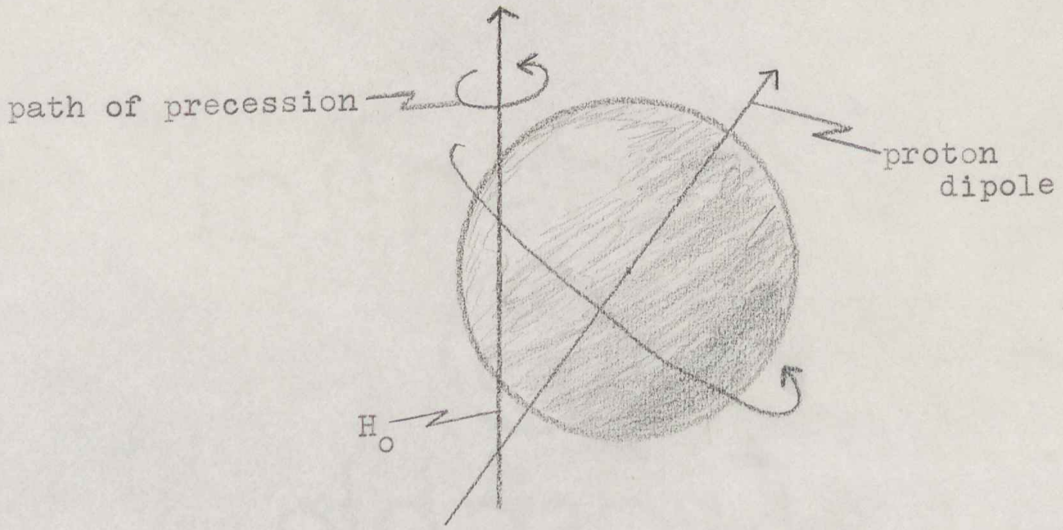


Figure 1. Proton in a magnetic field, dipole aligned with the field.

If external energy of a frequency attuned to the precessional frequency is applied to the system, the proton will "resonate" and flip into the higher energy configuration with a dipole aligned against the applied magnetic field. The change in magnetic susceptibility in this process is detected by the spectrometer and is shown as a peak on a potientiometric recorder.

A complication due to the rate of energy loss by the excited protons has proved to be very prominent in this particular study. Normally, the excited nuclei lose their excess energy to their environment by a process called spin-lattice relaxation. The rate of this energy loss is inversely related to the width of the peak determined by the nuclei. In solids, the process is very rapid and should result in a very narrow peak. In liquids, the process is not so rapid, but it is sufficient to give peaks of usable width. When a compound is in solid form, a second process becomes effective. In this process, the excited nuclei are able to pass their excess energy to each other with no net loss. This spin-spin relaxation causes the peak to broaden to such an extent that it is nearly useless from the standpoint of structure determination.

If a proton is in a magnetic field, the electron cloud surrounding it will also feel an effect from the applied field. These electrons will begin to circulate and create a second field just as a current in a wire. If the magnetic fields are considered as vectors, the nucleus "sees" the resultant of the applied and induced magnetic fields. If the nucleus "sees" an overall effect less than the applied field, it is said to be shielded. If the overall effect is greater than the applied field, the proton is deshielded. Protons in different environments are effected to different degrees by this induced field. The degree of shielding or deshielding is measured in reference to a standard tetramethylsilane absorption. Shielded protons absorb energy in a magnetic field near or higher than TMS and are said to be on the "upfield" end of the spectrum. Deshielded protons absorb energy at a much lower field than TMS and are consequently shifted "downfield."

To a first approximation, the effect of the electron cloud is dependent upon the electronegative effect of substituent groups on the molecule. However, this approximation does not hold for aromatic compounds. The protons in benzene absorb energy much further downfield than expected on the basis of electronegativity alone. Therefore, there must be another effect causing this large amount of deshielding. This other effect is due to the electrons which are delocalized into the pi cloud. Instead of circulating about a particular atom, they collectively flow around the radius of the ring. This type of circulation causes the induced magnetic field shown in Figure 2. From the diagram it can be seen that the benzene protons are in that portion of the ring's magnetic field that adds to the applied field, thereby causing deshielding. If it were possible to place a proton in the center of the plane of the molecule it would be expected to be strongly shielded,

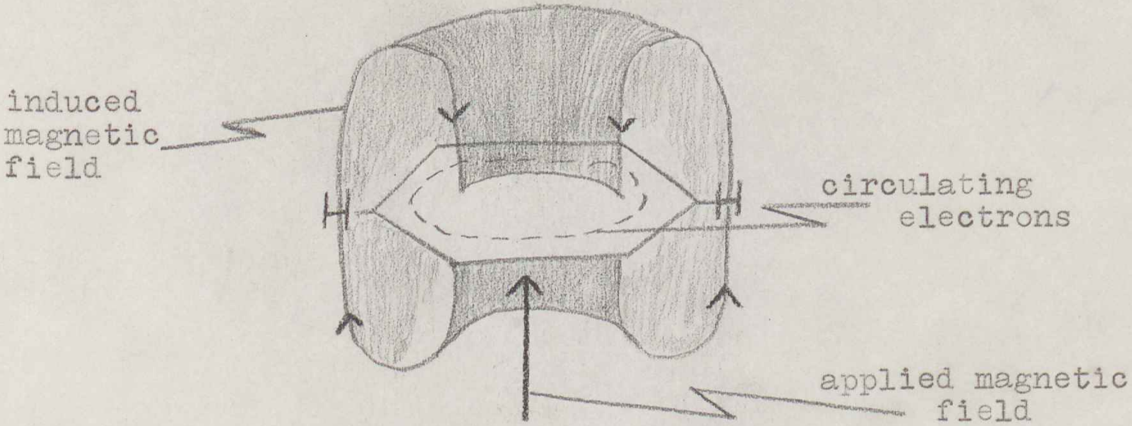


Figure 2. The benzene ring in a magnetic field and its induced magnetic field due to motion of electrons. (1)

and give an absorption in the upfield region of the spectrum.

Another aromatic compound, annulene (Figure 3) (18 pi electrons, therefore conforming to the 2n + 6 rule) demonstrates the shielding and deshielding effect of these systems more dramatically. The protons on the periphery of the ring absorb energy 8.9 ppm downfield from TMS and the inner protons absorb energy 1.8 ppm upfield from TMS. (2). This means that protons on the same ring have NMR absorbances that differ by 10.7 ppm.

Two other points to be mentioned briefly are:

1) The area under a peak due to certain protons is proportional to the munber of protons causing that peak. For example, diethyl ether, $CH_3CH_2OCH_2CH_3$, has two types of protons and shows two absorbances in its NMR spectrum. (Figure 4).

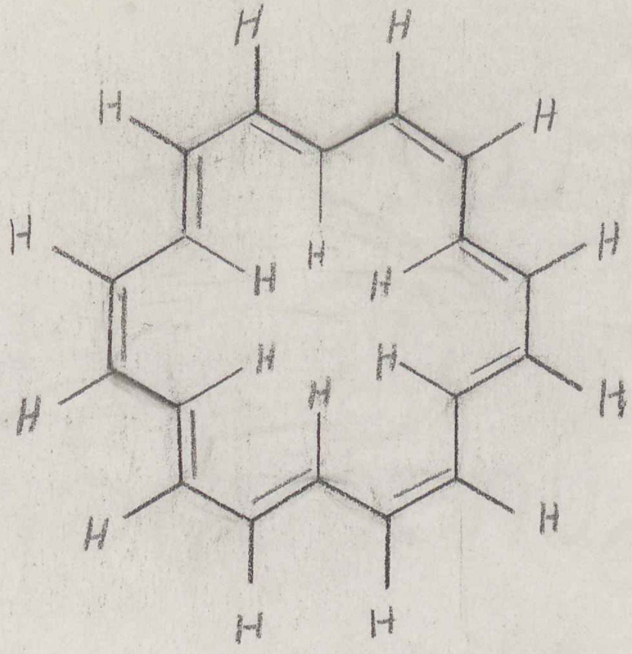
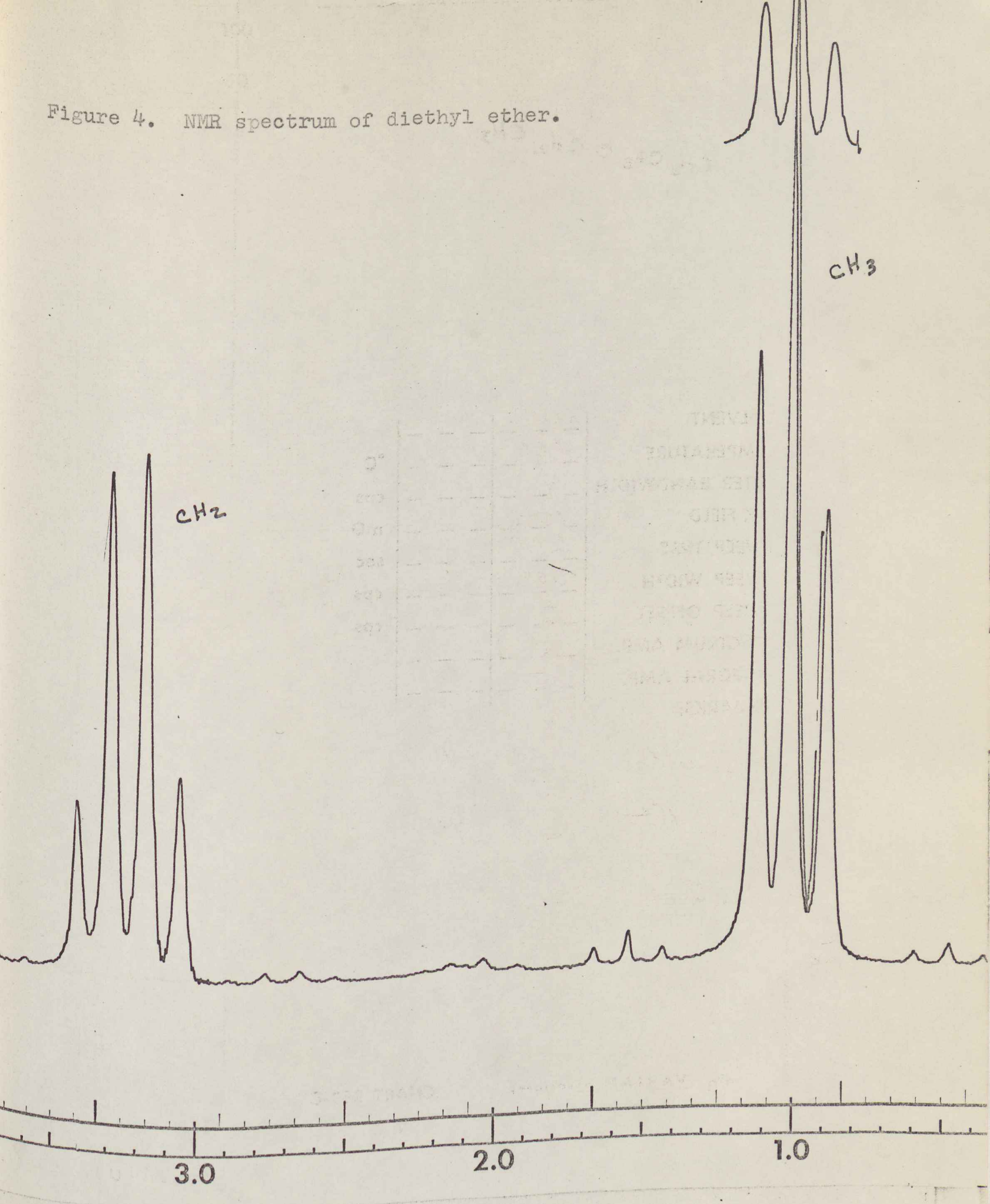


Figure 3. Annulene.

One absorbance is due to the six methyl protons and the other is due to the four methylene protons. Therefore, the peak areas should be in the ratio of 6:4 or 3:2.

2) If the carbon to which protons giving one absorption are bonded is also bound to a carbon containing magnetically different protons, the absorption will be split into one more peaks than there are neighboring protons. Again using diethyl ether as a model: the methyl protons have two neighboring methylene protons, and the methylene protons have the three neighboring methyl protons. It is therefore expected that the methyl absorption will be split into three peaks and the methylene absorption into four. (Figure 4).

Figure 4. NMR spectrum of diethyl ether.



Theory:

In the light of this background, consider the spectrum of diphenylmethane. (Figure 5). It shows only two types of absorption. The large peak at approximately 7.5 ppm (δ) is due to the ten aromatic protons and the smaller peak at 4.0 ppm (δ) arises from the two methylene protons. The ratio of peak areas, as expected is 5:1, and the lack of splitting indicates that there are no magnetically different protons on neighboring carbon atoms.

A closer inspection of the compounds actual structure might give the impression that perhaps the spectrum should not be so simple. (Figure 6).

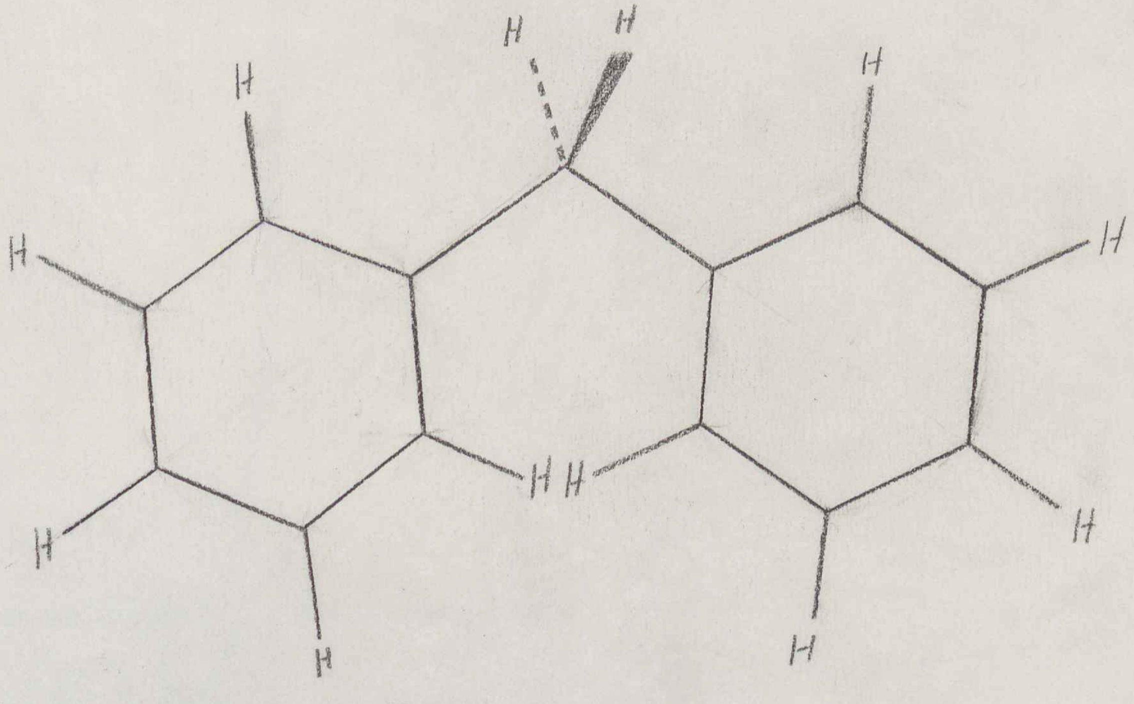
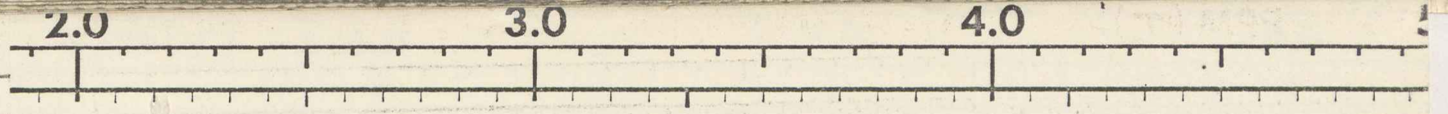


Figure 6. Diphenylmethane.

The ortho protons on either ring are beta to the methylene carbon while the meta and para protons are removed by three



400

Figure 5. NMR spectrum of diphenylmethane

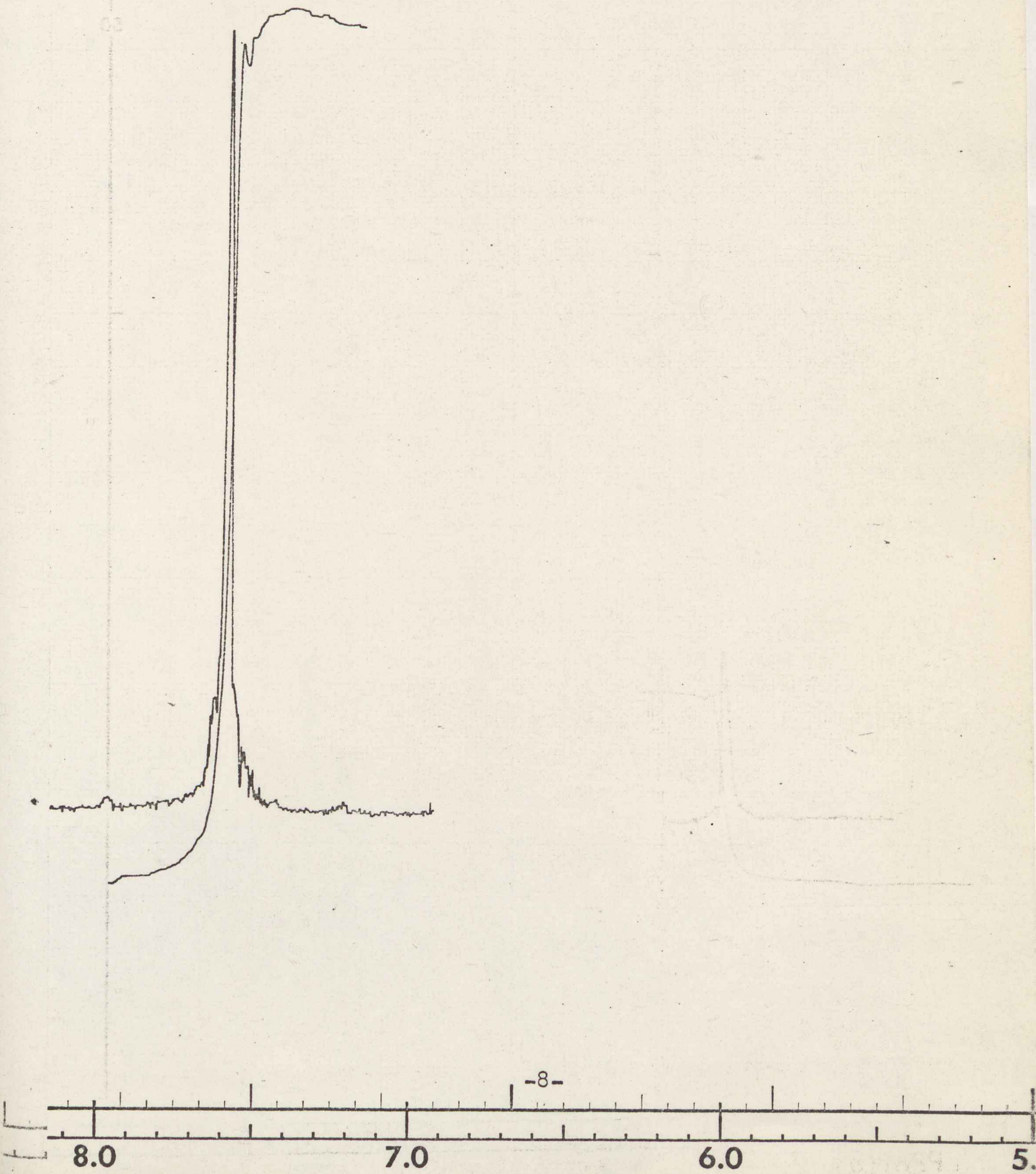
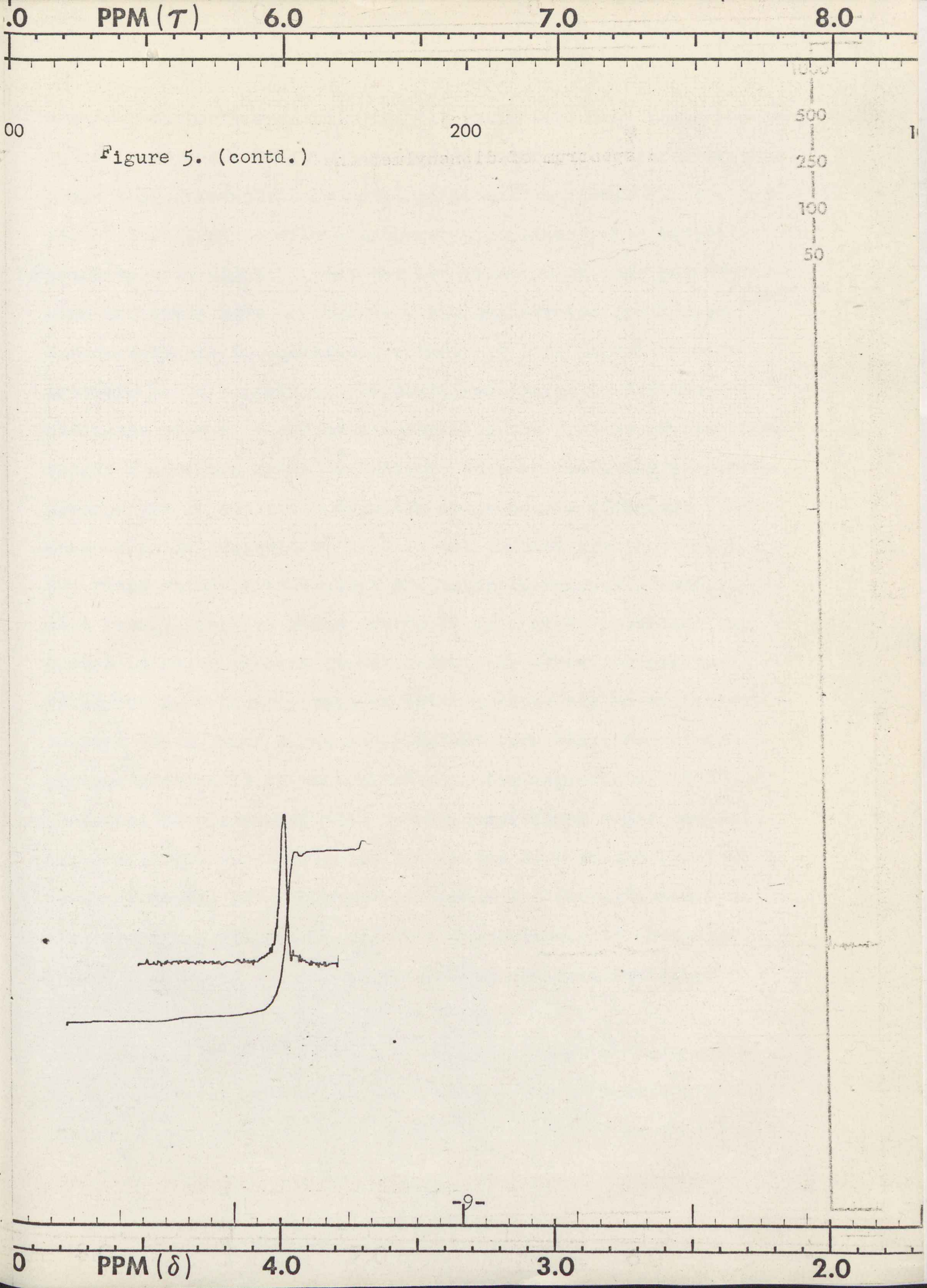


Figure 5. (contd.)



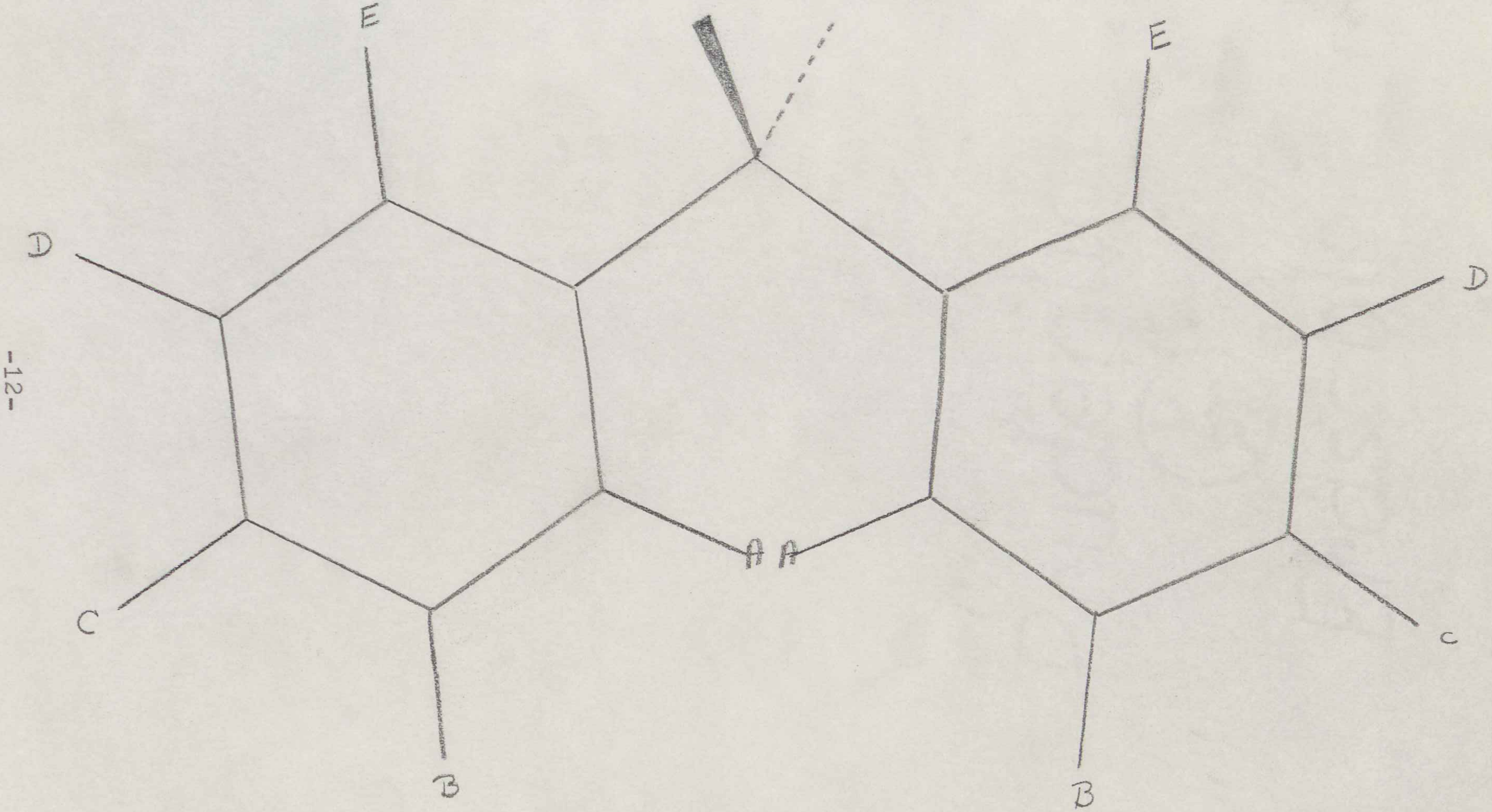
and four carbons, respectively. It would seem that there should be at least three different absorbances for the aromatic protons since they apparently are not magnetically equivalent. How then is the relatively simple spectrum rationalized? One possible consideration might be that the methylene group does not exert much influence over the magnetic field generated by the ring currents in the two benzene systems. If this is so then the aromatic protons might all be nearly equivalent. But what about the effect of one ring current on the protons of the other ring? The figure seems to indicate that at least the two ortho protons are in different magnetic environments (from one another). To account for this is the probability that the two rings rotate freely about the methylene-aromatic bonds. As a result, neither ortho proton is in a given position long enough to be considered distinct from the other. There is still the fact that though the ortho protons may be equivalent to each other, they might be different from the other ring protons because of their proximity to the magnetic field generated by the second ring. This possibility might account for the slight shouldering effect at the base of the aromatic peak. Probably the ortho protons are not different enough to give rise to a completely separate absorption. If there is any splitting, it is surely obscured by the overlapping of the peaks.

Having rationalized this spectrum by assuming free rotation of benzene rings, consider what might happen if rotation about the methylene-aromatic bonds was stopped. There are an infinite number of possible orientations of rings with respect to one another. The rings are likely to lock into a position with their planes separated by an angle of anywhere from 0° to 180°. To simplify the situation a qualitative judgement on three limiting cases of possible orientations can be attempted.

The first case is that in which the planes of the two rings are parallel to the plane formed by the two methylene-aromatic bonds. (Figure 7). The figure shows that there are five different types of aromatic hydrogens. If one could obtain a spectrum sensitive enough, it should show five absorptions. All the peaks would have the same area since they arise from two protons each.

Such an approach cannot be very realistic. What is more likely is that protons B, C, D, and E are far enough away from the influence of the other ring to be nearly magnetically equivalent. This is not the case with the A protons. The two are extremely close to one another. They appear so close, in fact, that it might be reasonable to assume that if one proton feels a strong deshielding effect from its ring, the other is likely to feel the same, or nearly the same, effect from that ring along with the effect from its own ring, consequently being "doubly" deshielded. If such is the case, a peak due to these ortho protons should appear much further downfield than the absorption due to the remaining eight protons, and the area ratios, ortho: meta-para: methylene, should be 1:4:1. For the aromatic absorptions the splitting pattern is likely to be quite conplex, since in an aromatic

Figure 7. Coplanar limiting conformation of diphenylmethane.

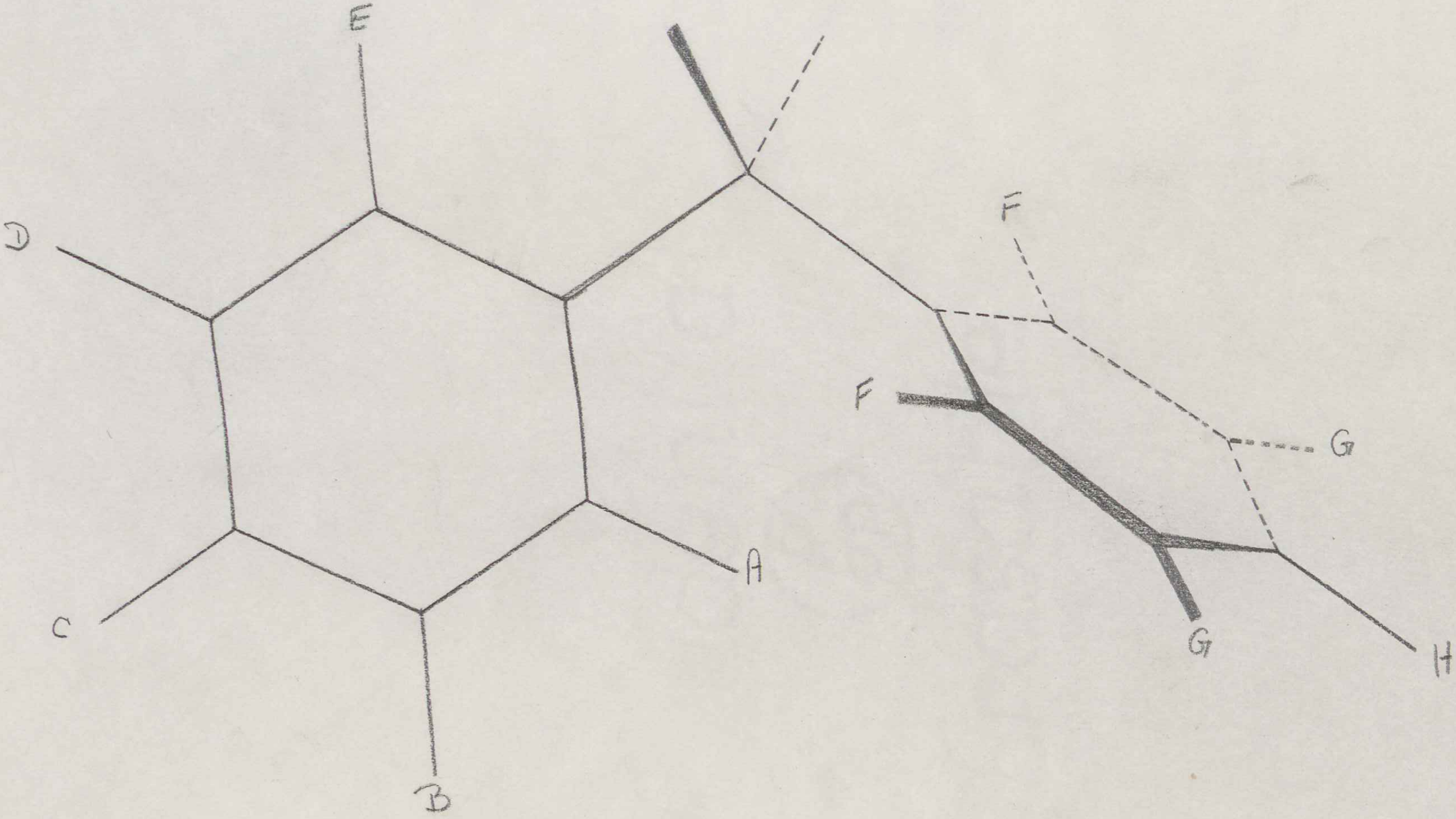


aromatic system a given proton is not only split by a magnetically different neighboring proton, but by all the magnetically different protons on the same ring. In addition, the effects of other ring protons which cause splitting can be combined in various ways, each one inducing still more splitting.

To obtain a picture of the second limiting case take one of the rings from the previous example and rotate it about its methylene bond 90° so that its plane is perpendicular to that of the other ring and the plane of the two methylene-aromatic bonds. (Figure 8). A naive approach calls for eight different absorptions. The area under the F and G peaks should be twice that of any other aromatic peak since these peaks arise from two protons each as opposed to the other single-proton peaks.

More realistically one is likely to find that the B, C, D, E, G, and H protons are almost equivalent. It is difficult to speculate on whether the A and F protons feel any effect of ring currents other than their own, and whether this effect is the same for both or different enough to give rise to distinguishable peaks. The first option, the A and F protons feeling no effect outside that of the ring on which they are located, would give a spectrum very similar to that of the free rotation one, since it has all the aromatic protons equivalent. This means that it would be impossible to determine whether or not the rings have actually stopped rotating at all. A second possibility is that the A and F protons feel

Figure 8. Planar - perpendicular limiting conformation of diphenylmethane



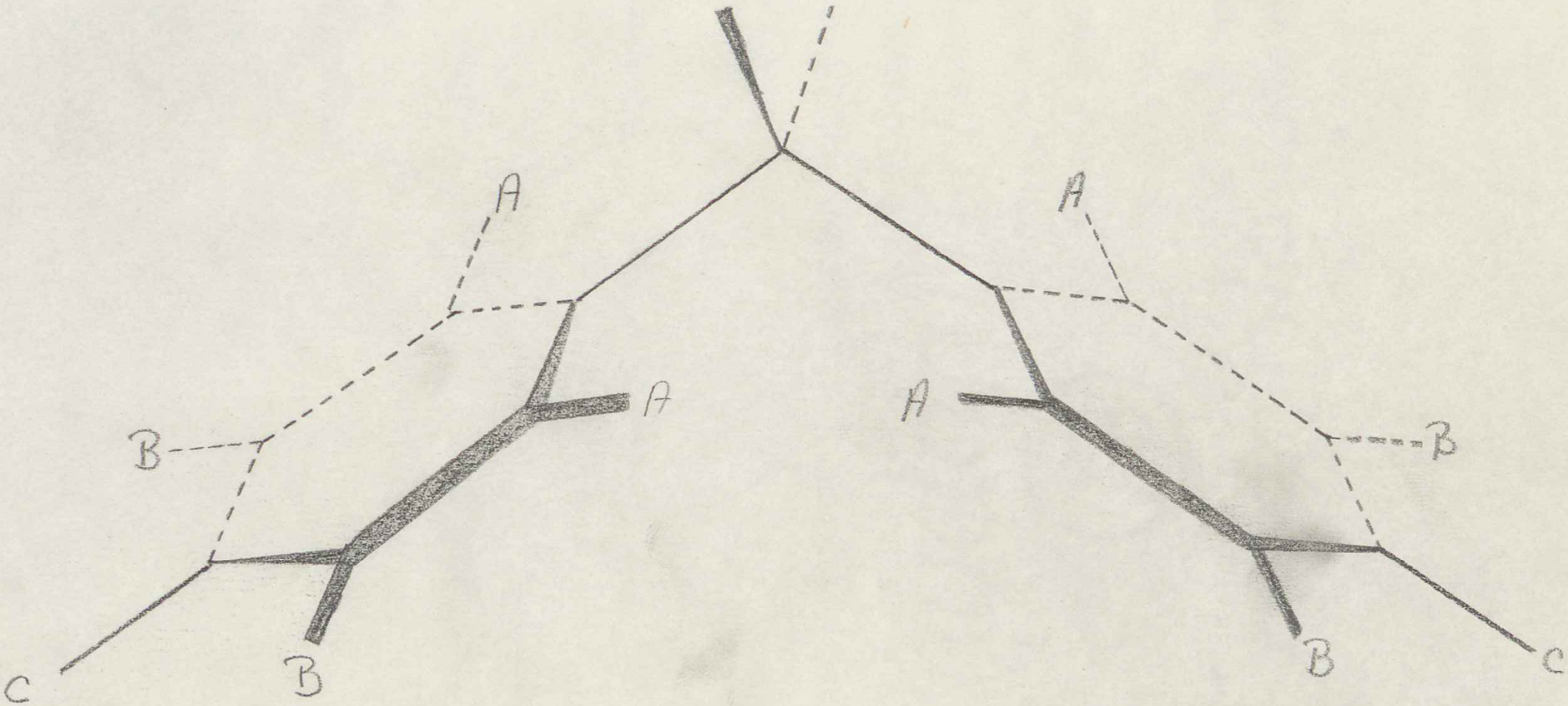
roughly the same influence from opposite rings. This would result in two aromatic absorptions, in the ratio of 3:7. The third possibility is that the A and F protons are affected differently by each other's ring and are both different from the remaining aromatic protons. In this case three aromatic absorptions would occur in the ratio of 1:2:7.

The third limiting conformation is the one in which both benzene rings are rotated 90° out of the plane of the methylene-aromatic bonds. (Figure 9). In an ideal case there are only three distinguishable types of hydrogens. The three absorptions should be in the ratio ortho: meta: para: of 2:2:1.

More realistically, the B and C protons are likely to be almost equivalent and inspection of the figure does not give any hint as to whether the A protons feel any effect from the opposite ring. If one goes on the assumption that the ortho protons are free from any effect other than that of their own ring, the expected spectrum would be similar to that of the free rotation spectrum. The possibility that these protons do feel an influence from the opposite ring's magnetic field means that the aromatic hydrogens would absorb in two different positions. The peak ratios, ortho:meta-para would be 2:3.

It is obvious that any attempt to determine a rotational isomer from qualitative considerations alone would prove inconclusive, even if the three limiting cases were the only ones possible. Furthermore, there is no hope of distinguishing

Figure 9. Coperpendicular limiting conformation of diphenylmethane.



one intermediate conformer from others similar to it by inspection alone.

The premise that NMR is a useful tool for this study is based on the calculations of Johnson and Bovey (3,4). They have compiled a table of the effect of the magnetic field of a benzene ring with respect to position. The shifts they have calculated are measured in ppm upfield or downfield from the absorption of a corresponding ethyleneic proton. For example, the methyl protons of toluene would be measured from the reference peak given by the methyl protons in 1-propene. (Figure 10). Diphenylmethane's ethyleneic analog is allyl

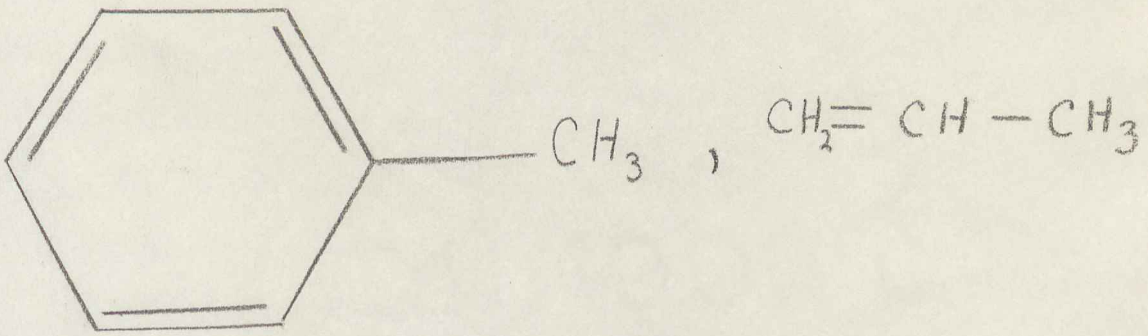


Figure 10. Toluene and its ethyleneic analog, 1-propene.

benzene. (Figure 11). To reference position, Johnson and Bovey used cylindrical coordinates, basing their calculations

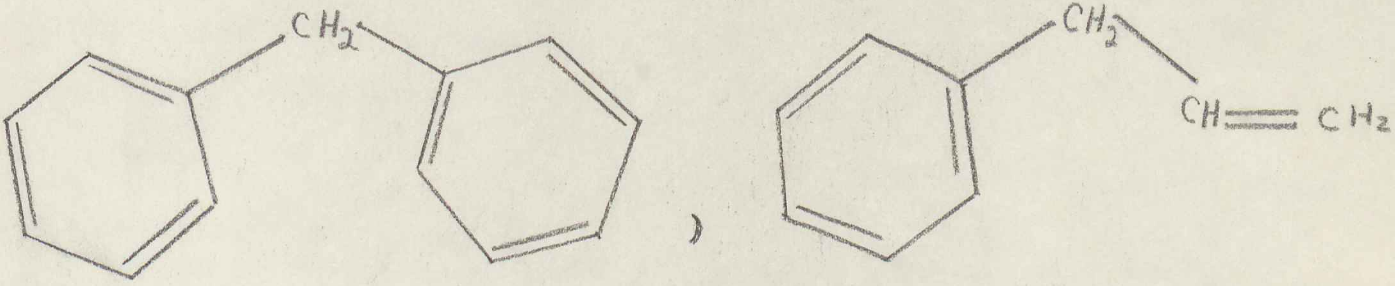


Figure 11. Diphenylmethane and its ethyleneic analog, allyl benzene.

on two parameters. Using the plane of the ring as a base, and the center of the ring as an axis, they tabulated results of their calculations in terms of distance from the axis in the plane of the ring (rho) and height above the plane (z). The unit of length used was a "ring radius", which is 1.39 A.

Using simple solid and plane geometry it is possible to calculate the position of any proton in diphenylmethane with respect to either ring in each of the limiting cases. Probably the most useful calculation would be for ortho protons of one ring in reference to the opposite ring. More specifically, for the ortho proton that is likely to feel the greatest effect from the other ring's magnetic field.

The geometry consists of constructing a series of right triangles, and using known bond lengths and angles to calculate a series of inter-atomic distances, culminating in determination of the rho and z coordinates. An example of how this geometry works can be seen in the calculations for the limiting conformations of diphenylmethane (Figures 12, 13, 14).

A = methylene carbon
B = carbon of first ring bonded to methylene carbon
C = carbon on first ring ortho to methylene attachment
D = proton for calculation
E = carbon on second ring bonded to methylene carbon
F & G = ortho carbons on second ring
F' = meta carbon on second ring

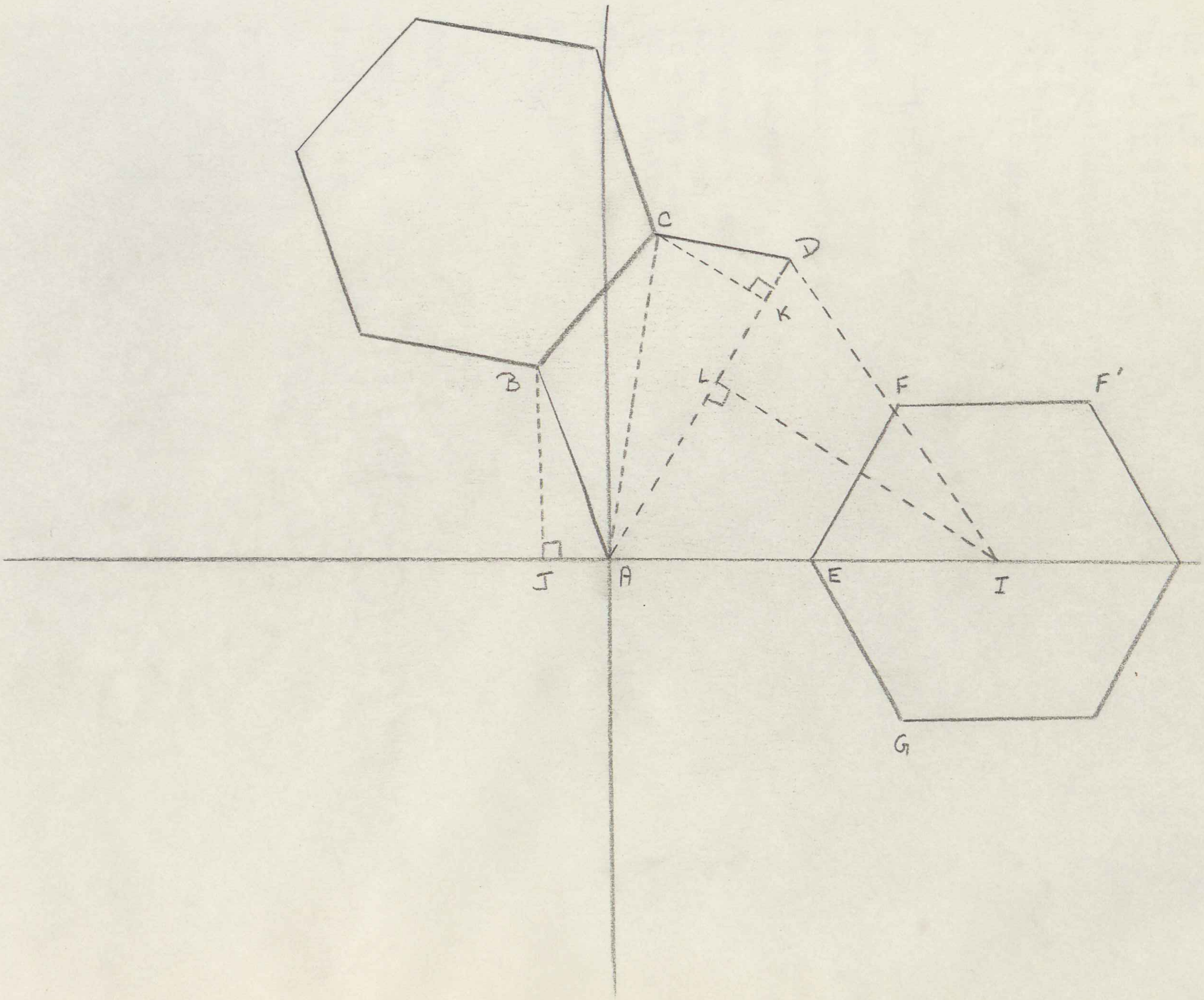
Construct triangle ABJ: angle AJB is a right angle
$\angle JBA = 180^\circ - \angle ABC$
$JA = AB \sin \angle JBA$
$JB = AB \cos \angle JBA$
$JC = JB + BC$
$AC = (JA^2 + JC^2)^{\frac{1}{2}}$

Construct triangle CDK: $\angle CKD$ is a right angle
$\angle BCA = \arctan JA/JC$
$\angle ACD = \angle BCD - \angle BCA$
$KC = CD \cos \angle ACD$
$AK = AC + KC$
$DK = CD \sin \angle ACD$
$AD = (AK^2 + DK^2)^{\frac{1}{2}}$

Draw lines EI and FG intersecting at H.
Assume that they are perpendicular.
$\angle FEH = \frac{1}{2} \angle FEG$
$EH = EF \cos \angle FEH$
$HI = \frac{1}{2} FF'$
$EI = EH + HI$
$AI = AE + EI$

$\angle CAD = \arctan DK/AK$
$\angle BAC = 180^\circ - \angle ABC - \angle BCA$
$\angle DAE = \angle BAE - \angle BAC - \angle CAD$

Figure 12. Coplanar conformation on coordinate system.



Construct triangle LID: angle DIL is a right angle
$AL = AI \cos \angle DAE$
$DL = AD - AL$
$IL = AI \sin \angle DAE$
$DI = (IL^2 + DL^2)^{\frac{1}{2}}$

For the coplanar conformation (Figure 12):

$\text{rho} = DI$
$z = 0$ (both ring are in the same plane)

In the second limiting conformer, with one ring rotated 90° out of the plane, the distances of the ortho proton from the methylene carbon and from the center of the rotated ring remain the same.

Construct triangle IMD: angle DMI is a right angle
$AM = AD \cos \angle DAE$
$IM = AE - AM$
$DM = AD \sin \angle DAE$

For planar-perpendicular conformation (Figure 13):

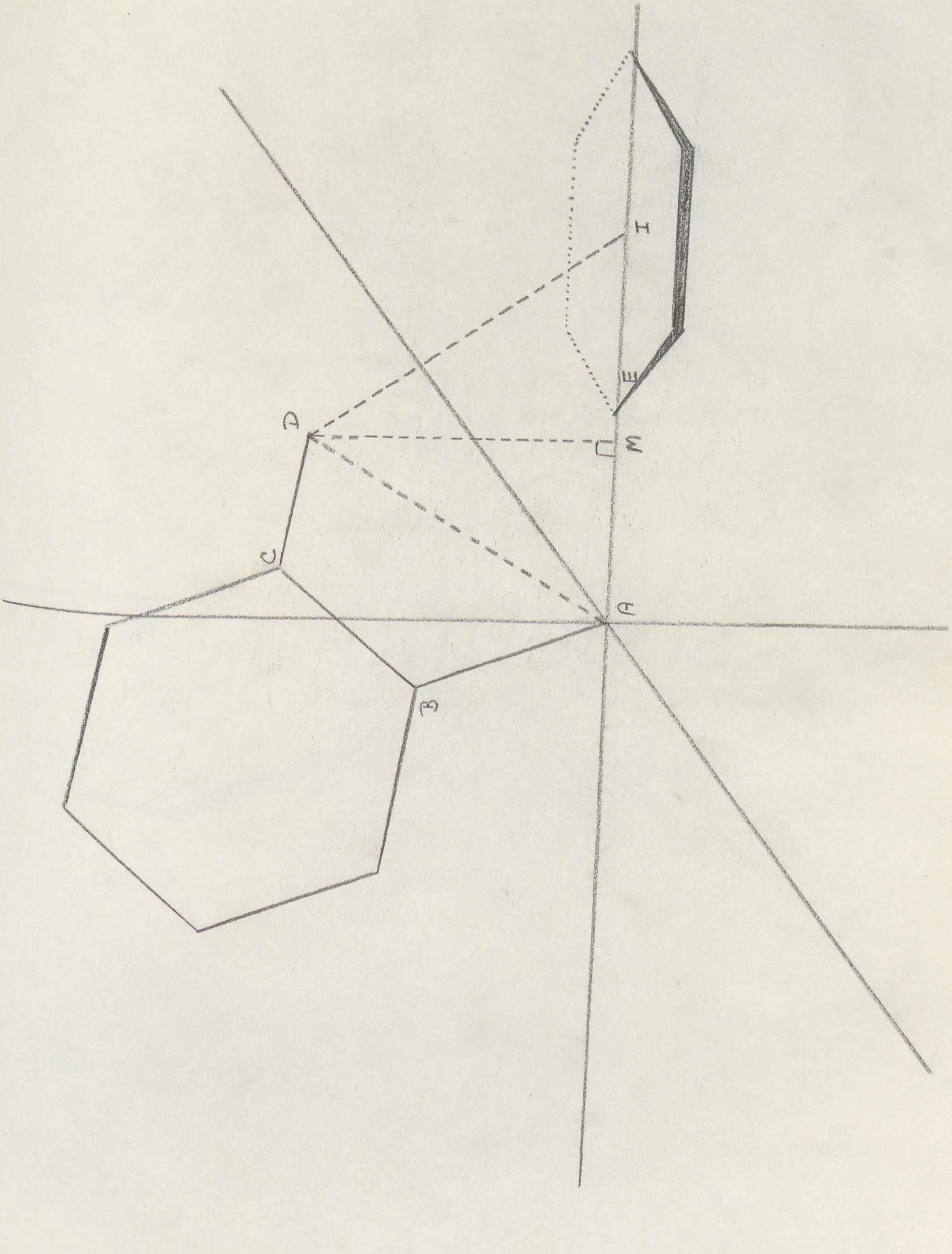
$\text{rho} = IM$
$z = DM$

For the third limiting case, both rings rotated out of the plane, the assumption that the distance of the ortho proton from the methylene carbon does not change is made.

The projection of AD on the yz plane is AQ
$\angle BAD = \angle BAC + \angle DAC$
$AQ = AD \cos \angle BAD$
$\angle RAQ = 180^\circ - \angle BAE$
$RQ = AQ \sin \angle RAQ$
$AR = AQ \cos \angle RAQ$
$IR = AI + AR$
$DQ = AD \sin \angle BAD$
$RS = DQ$
$SI = (IR^2 + RS^2)^{\frac{1}{2}}$

For the coperpendicular conformation (Figure 14):

$\text{rho} = SI$
$z = RQ$



-perpendicular conformation on coordinate axis.

Figure 13. Planar-perpendicular conformation on coordinate axis.

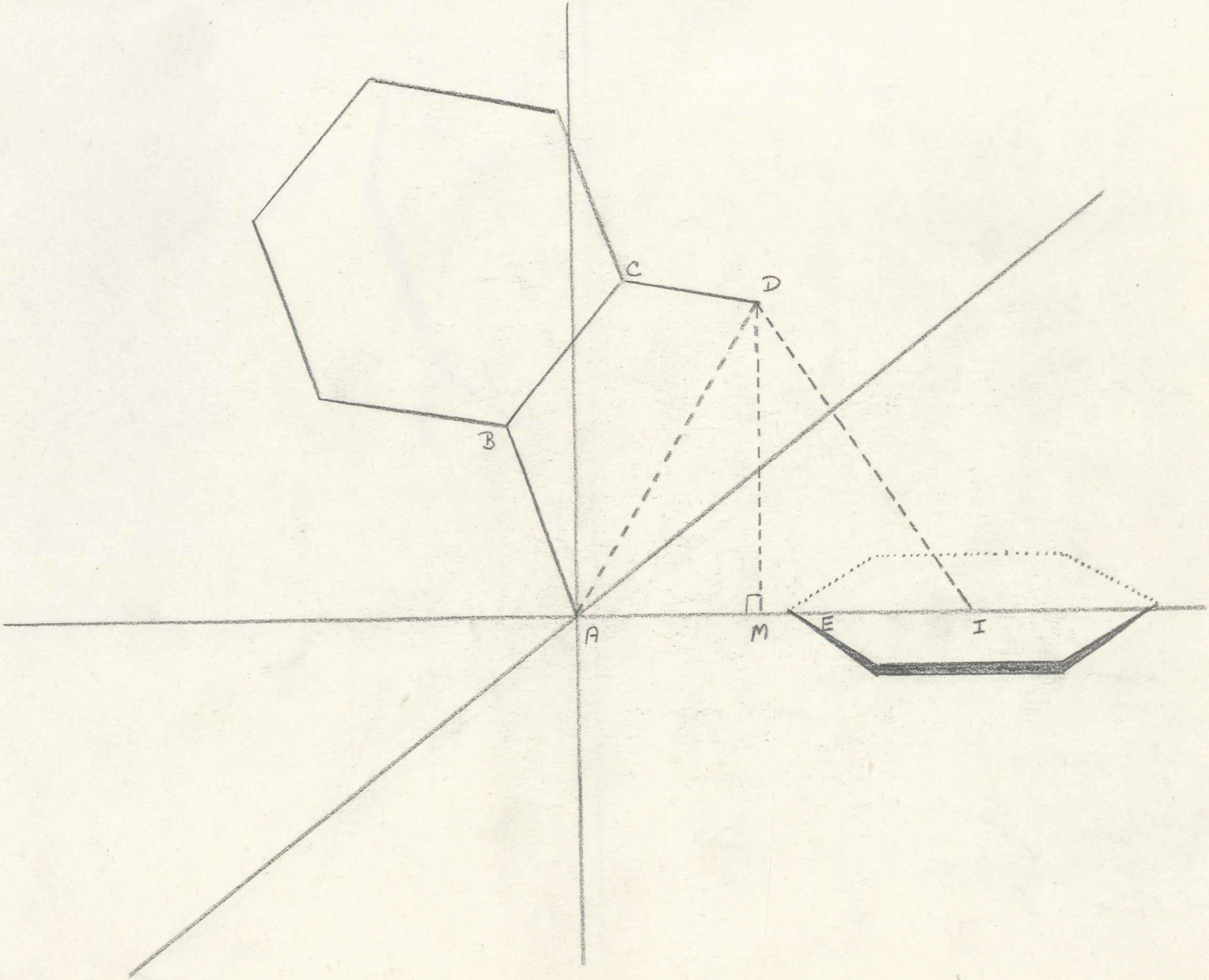
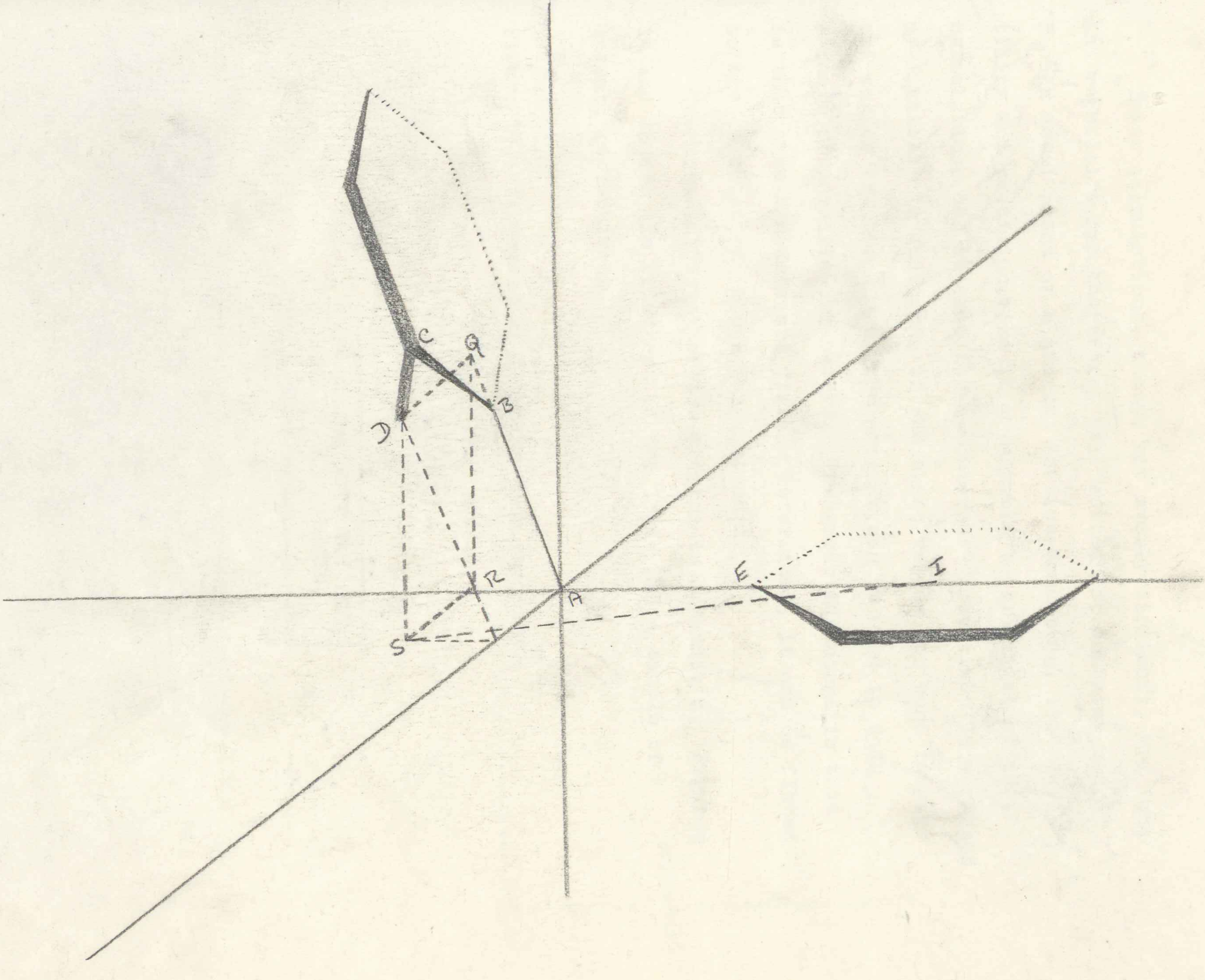


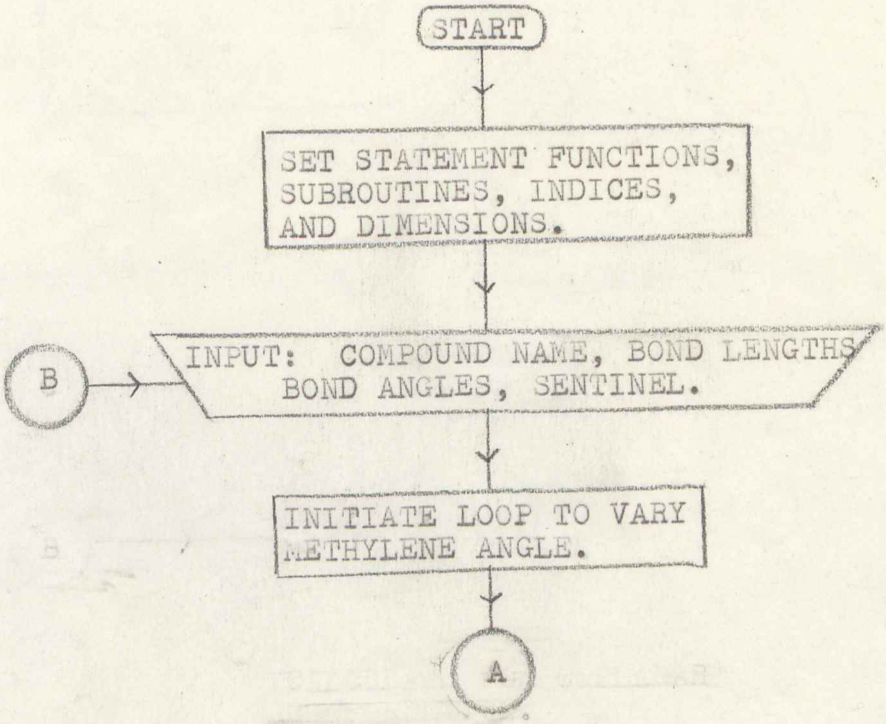
Figure 14. Coperpendicular conformation on coordinate axis.



These calculations, though not overly difficult, are long and repetitive and therefore, well suited for computer use. Though development of a program is time-consuming, its versatility and precision make it a valuable tool. First of all, calculations can be made for a number of derivatives in a matter of minutes. In addition, if the exact values for bond lengths and angles are not known, the program can be used to scan a range of possible parameters. The great advantage in this is that when NMR data are finally determined, it can be fitted to the calculation in the range scanned.

The actual listing of the program is Appendix A. Figures 14 and 15 are the flowchart of the logic and a sample of output, respectively.

Figure 14. Flowchart of limiting case geometry.



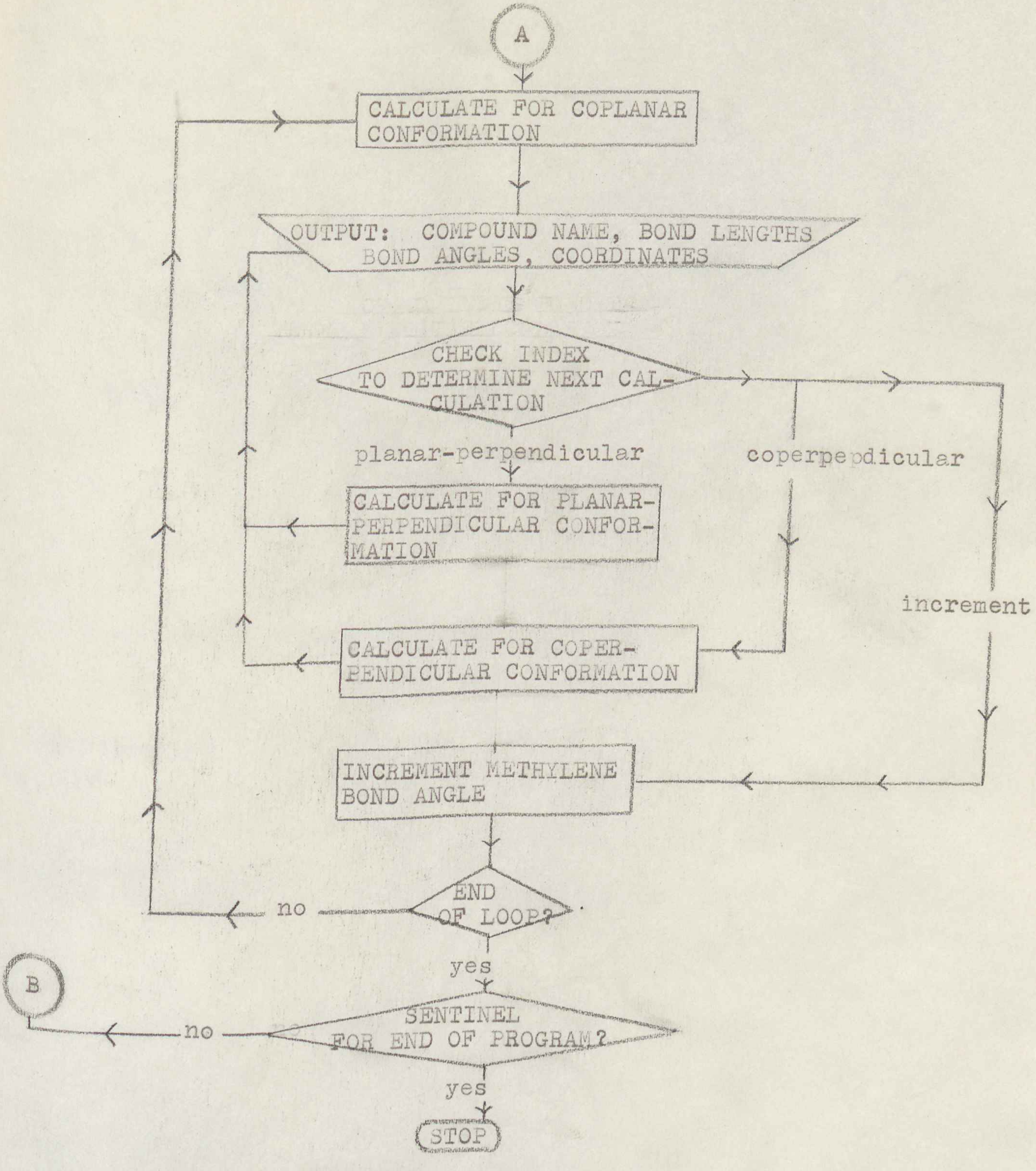

A
CALCULATE FOR COPLANAR CONFORMATION
OUTPUT: COMPOUND NAME, BOND LENGTHS BOND ANGLES, COORDINATES
CHECK INDEX TO DETERMINE NEXT CALCULATION
planar-perpendicular
coperpepdicular
increment
CALCULATE FOR PLANAR-PERPENDICULAR CONFORMATION
CALCULATE FOR COPERPENDICULAR CONFORMATION
INCREMENT METHYLENE BOND ANGLE
END OF LOOP?
no
yes
B
SENTINEL FOR END OF PROGRAM?
no
yes
STOP

Figure 15. Sample output from computer program calculating geometry for limiting cases.

```
IPHENYLMETHANE


     KNOWN VALUES



           XAB=1,5300                           ANGBAE=1.9020

           XBC=1,3900                           ANGABC=2,0940

           XCD=1,0800                           ANGBCD=2.0940

           XAE=1,5300                           ANGFEG=2,0940

           XEF=1,3900

           XFFP=1.3900






     CONFORMATION                      RHO                         Z


          COPLANAR                   1,9477                     0,0000
  PLANAR-PERPANDICULAR               1.0401                     1,6468
        COPERPANDICULAR              2,9320                     1.1461



UPPLEMENT

DQ=
      2,1388
QR=
      1,5931
AR=
      0,5490
DM=
      2.2891
AM=
      1.4745
IR=
      3,4692
RS=
      2.1388
RM=
      2,0235
```

The bond length and angle data used as input for the program is mostly based on inference and assumption. Values available for known compounds (5) were modified to fit the diphenylmethane derivatives for which no experimental data were available. For example, the aromatic C-C bond length in diphenylmethane is assumed to be the same as that in benzene and toluene, the methylene-aromatic bond length is taken to be the same as that for 3,3' dichloro 4,4' dihydroxydiphenylmethane. (Figure 16).

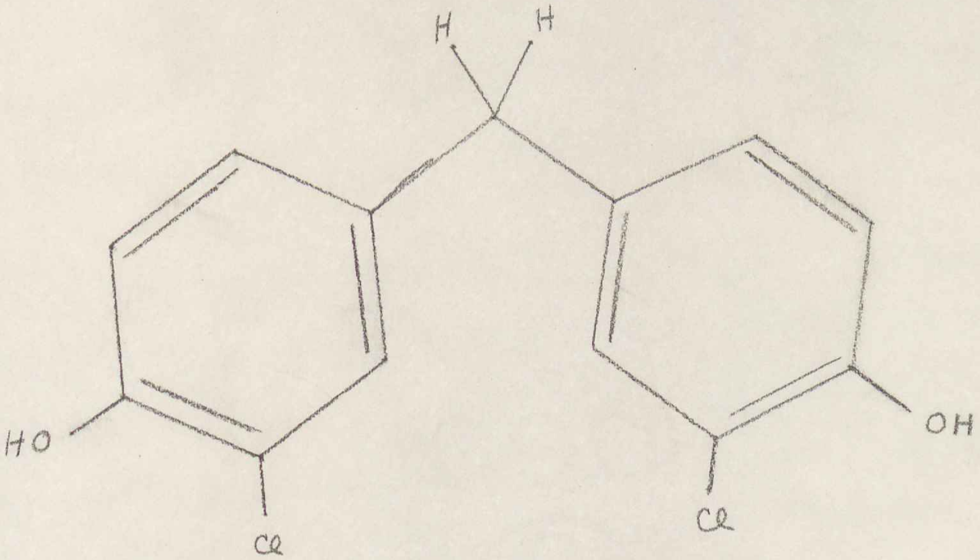


Figure 16. 3,3' Dichloro, 4,4' dihydroxydiphenylmethane.

Working with the values assigned to diphenylmethane, data for its various derivatives were obtained by inferring that the substituents had roughly the same effect on the bond length of the unknown compounds as they do on known compounds. For example, if two chlorine molecules are placed on a methane molecule the remaining C-H bonds are shortened to approximately 97% of their original length. (Therefore) it was assumed that for dichlorodiphenylmethane the methylene-aromatic bonds would be shortened by the same amount. The same general procedure was followed for all the derivatives used.

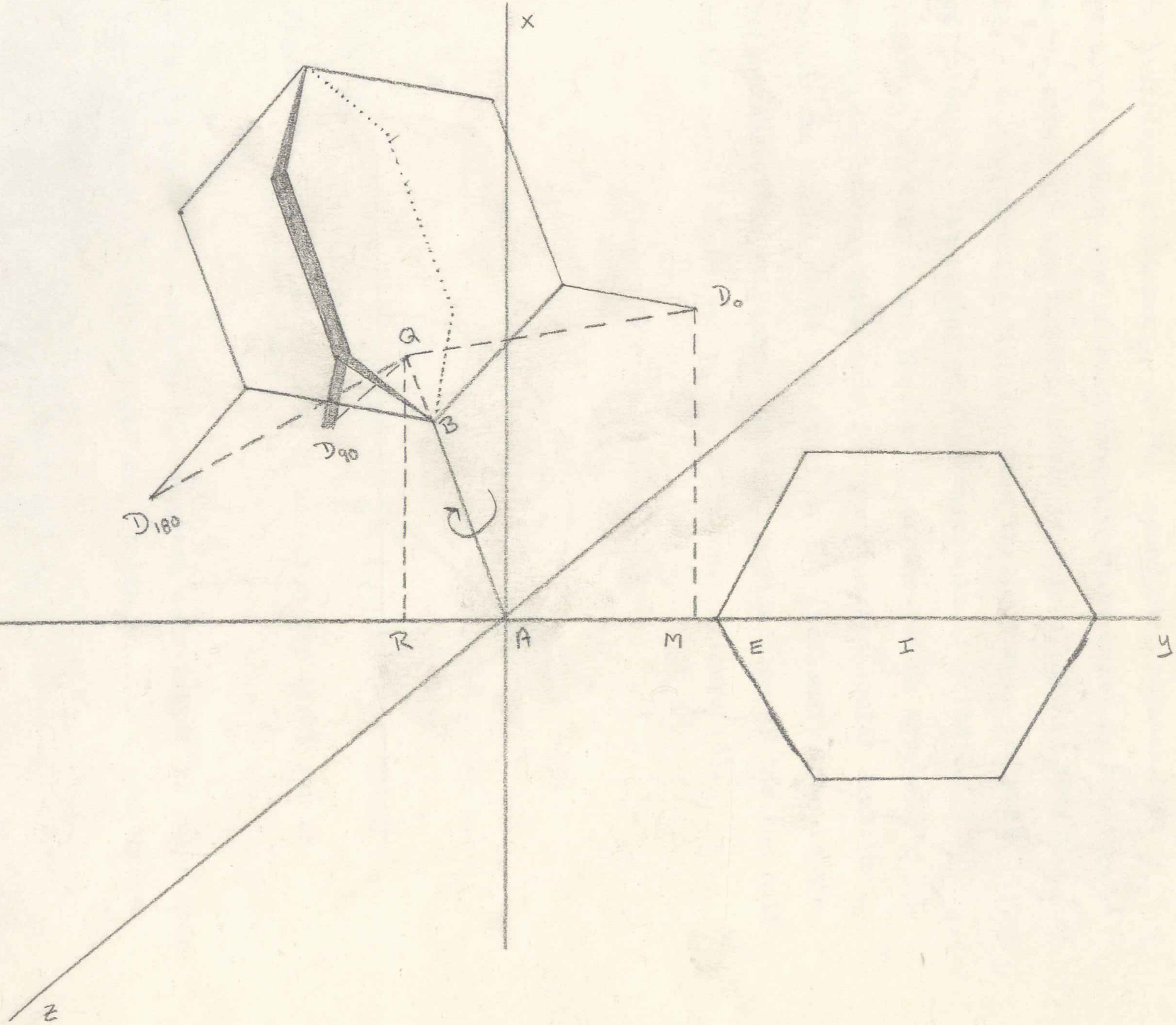
Perhaps the most serious inaccuracy occurs in the assignment of values to the angle made by the two methylene bonds. Other than X-ray studies or some other means of determining interatomic distances and angles, there is no way of knowing how the presence of the rings on the methylene carbon affect the angle, especially when there are substituents other than hydrogen on the same carbon. To accomodate this complication the program is used to consider values of this angle at various points in a ten degree range above and below the assigned value.

With this first program it is possible to calculate the coordinates for all three limiting cases. Values for the intermediate cases must still be determined. The intermediate conformations are considered for the two simplest of the infinite number of possible sets. 1) One ring is considered to remain stationary in the plane of the methylene bonds, and coordinates for the second ring are calculated at various points in its rotational path about its methylene-aromatic bond. 2) The ring that was stationary in the methylene bond plane is rotated 90° and considered stationary in this new position; the second ring is again rotated about its methylene bond and calculations made as before. The geometry here becomes somewhat more involved than for the limiting cases.

Case 1 (Figure 17):

The ring with its center at point I is the one that will

Figure 17. Intermediate cases of rotation for diphenylmethane, stationary ring in plane.



be considered stationary. As the second ring rotates, the proton for which the calculations are to be made, D, traces out a circle in space. The radius of this circle is length DQ, the perpendicular distance from the proton to the axis of rotation. The center of this circle is at point Q. The location of point Q and the length of the radius are both known from calculations made for the coperpendicular limiting case. The height above the plane of the stationary ring is the height above the xy plane. Consider a side view of the top half of the circle described by the D proton. (Figure 18).

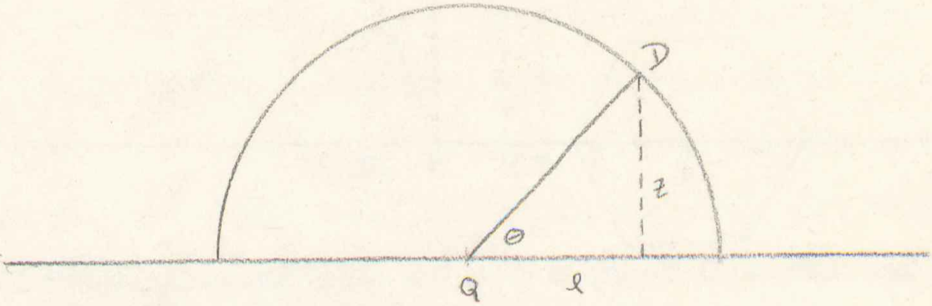


Figure 18. Side view of path of rotation for first set of intermediate cases.

θ is the angle of rotation that a given calculation is being made for. Knowing this and the radius, length DQ, the z coordinate can be determined

$$z = DQ \sin \theta \qquad (l = DQ \cos \theta).$$

The set of rho coordinates for all the possible angles of rotation is given by the projection of the circle on the plane of the stationary ring, the xy plane. The rho coordinate for the coplanar limiting case is already known. The position of point Q with respect to the center of the stationary ring can be readily obtained. Its distance from point I is the hypotenuse of the triangle IQR and sides IR and QR have already been determined. Now, since two points on the line that is the set of rho coordinates are known it is a simple matter to determine the equation of the projection. (Figure 19).

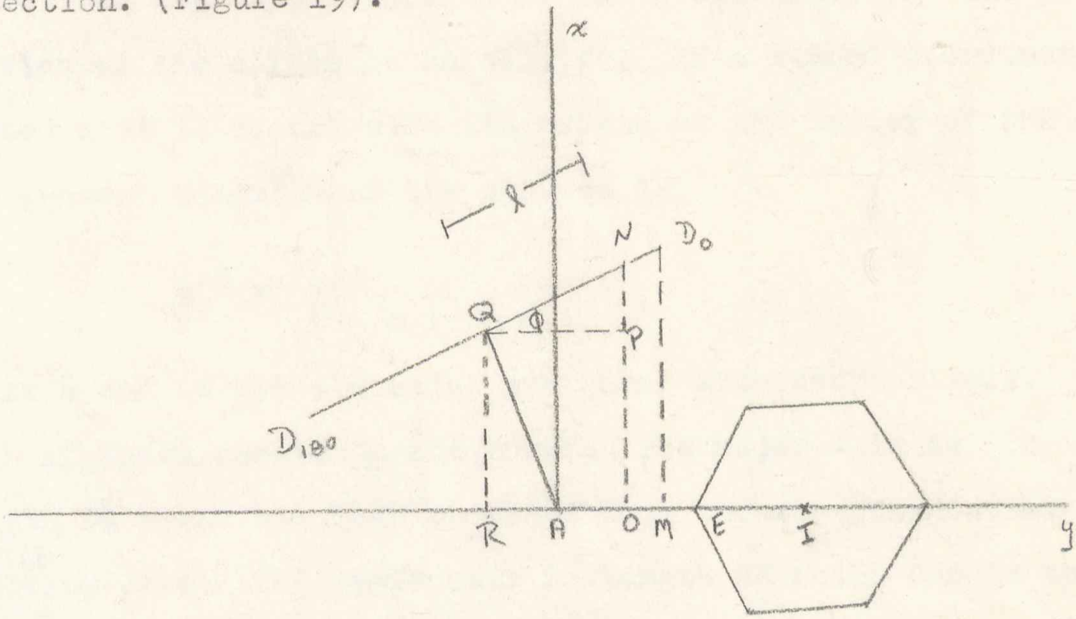


Figure 19. Projection of path of rotation of D proton on the xy plane.

For a given angle of rotation the rho coordinate is the distance NI. The slope of the line form the projection, D_0D_{180} is

$$\frac{D_oM - QR}{AM + AR}$$

D_oM has been determined in the planar-perpendicular case
AM has been determined in the planar-perpendicular case
AR has been determined in the coperpendicular case

$\tan \Phi = (D_oM - QR)/(AM + AR)$
$NP = l \sin \Phi$
$NO = QR + NP$
$QP = l \cos \Phi$
$QI = RI - QP$
$\text{rho} = (\overline{NO}^2 + \overline{OI}^2)^{\frac{1}{2}}$

Case 2 (Figure 20):

The second set of intermediate rotational isomers is more complex than the first. Consider the rho coordinate. The set of all the rho coordinates is the projection of the circle traced out by the D proton on the xy plane. (Note that the coordinate system has been shifted in such a way as to keep the z axis coincident with the direction of the z coordinate). The projection of the circle is an ellipse. If a second coordinate system x'y' is placed with its origin at the center of the ellipse, the general equation of the ellipse is

$$\frac{x'^2}{a^2} = \frac{y'^2}{b^2} = 1$$

where a and be are the major and minor axis respectively. Both of these constants are known. The major axis is (simply) length DQ which has been obtained from the coperpendicular limiting case. The minor axis is length RM which can be calculated from values obtained from the coperpendicular and planerperpendicular cases. Knowing the a and b values, we can plot the projected ellipse. Figure 21 is this plot. In this diagram θ is the angle of rotation. The specific rho coordinate for this angle is the distance from the point where the line intersects the ellipse to the center of the stationary ring. The slope of the line is tan $(90^\circ - \theta)$ and its equation, therefore is

$$y' = [\tan(90^\circ - \theta)]\, x'.$$

Solving simultaneous equations gives the point of intersection.

$$y'^2 = [\tan^2 (90^\circ - \theta)]\, x'^2$$

$$\frac{x'^2}{a^2} + \frac{[\tan^2 (90^\circ - \theta)]\, x'^2}{b^2} = 1$$

Figure 20. Intermediate cases of rotation for diphenylmethane, stationary ring out of plane.

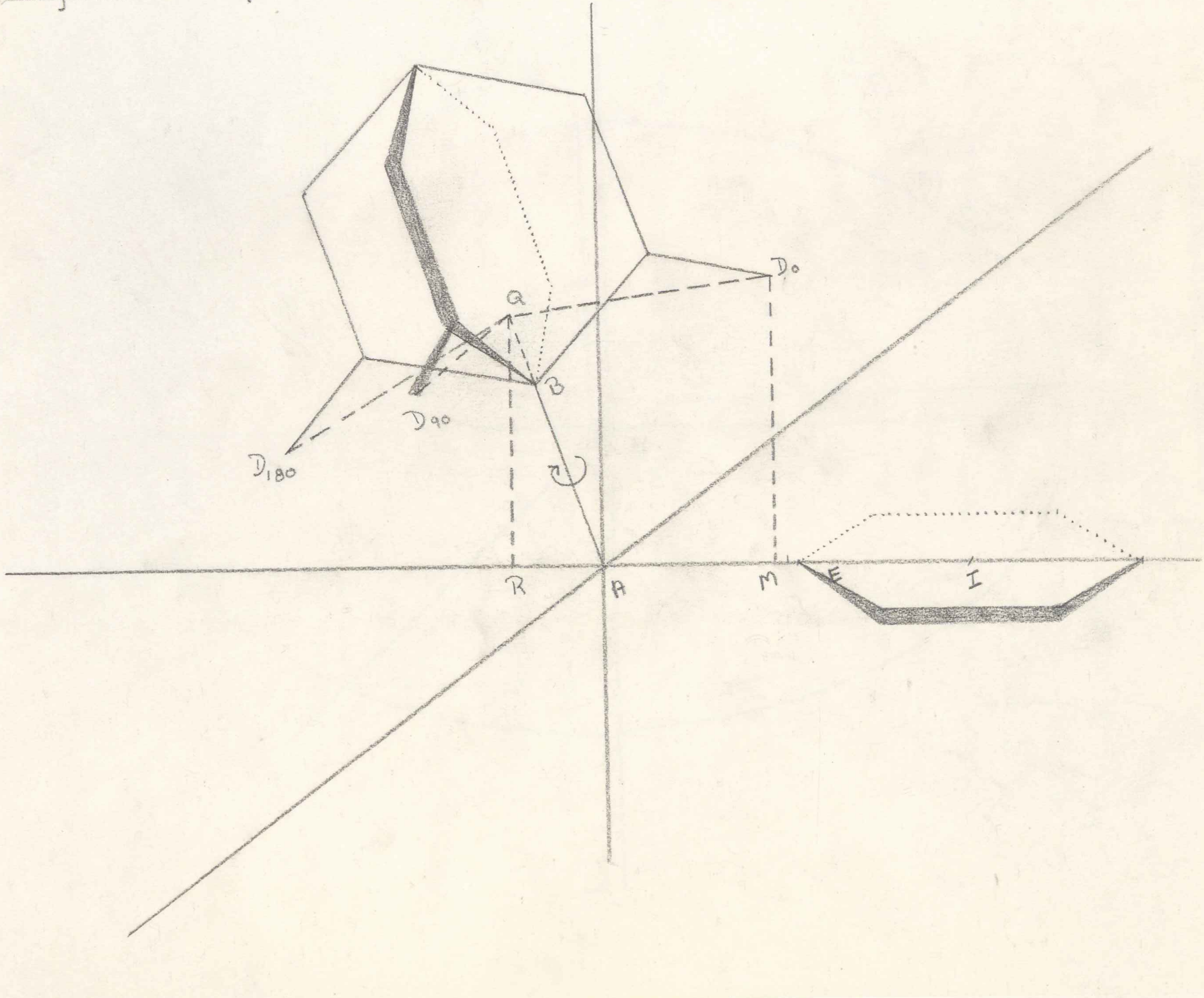
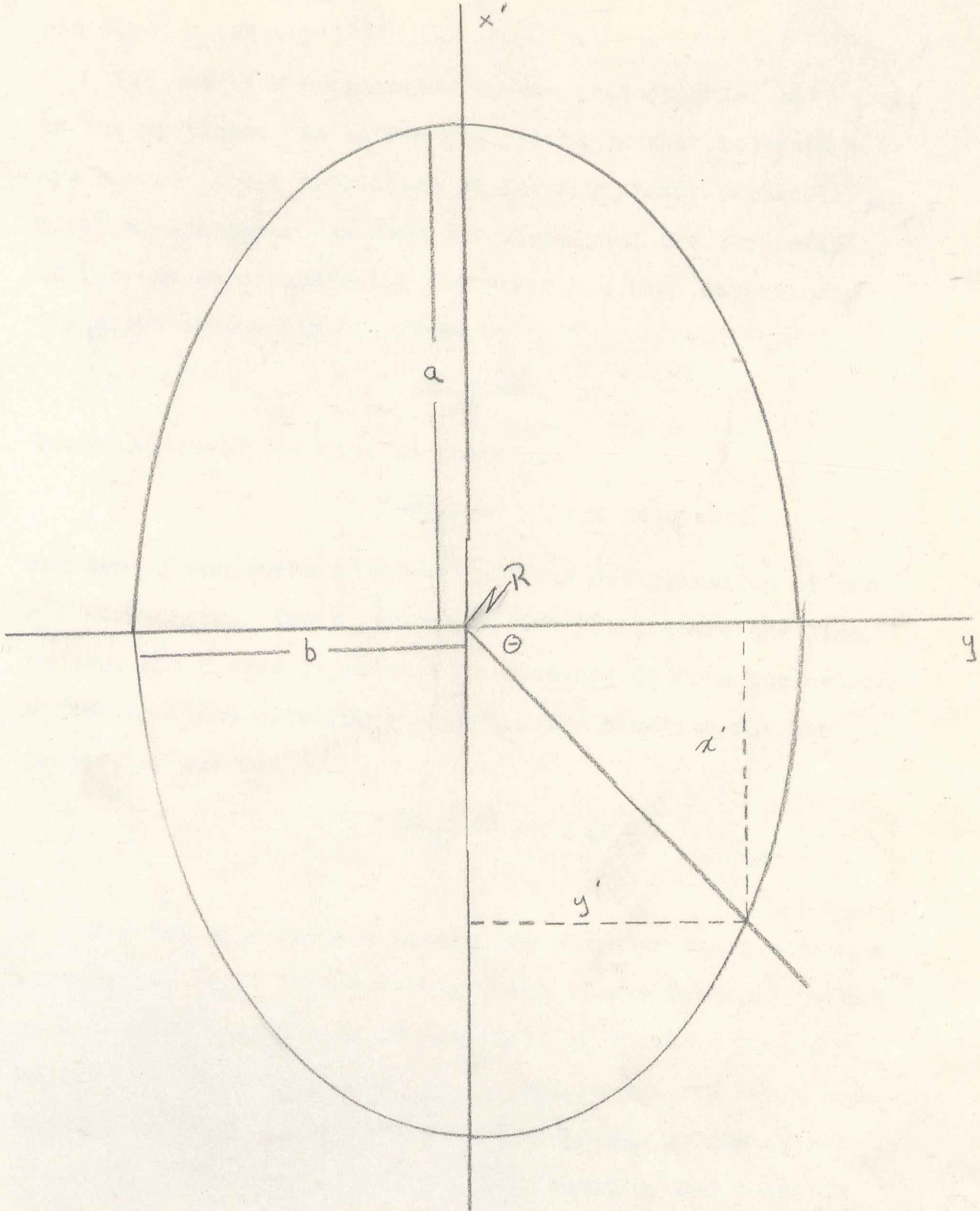


Figure 21. Projection of circle in case 2 of intermediate conformations on xy plane.



$y' = [\tan(90^\circ - \theta)]\, x'$

$\text{rho} = (x'^2 + (RS - y')^2)^{\frac{1}{2}}$

The set of z coordinates is the projection of the circle on the yz plane. As before two points on the projected line are known. The z coordinate DM for the planar-perpendicular limiting conformer has been calculated and the z coordinate QR for the coperpendicular conformer has been determined. The slope of the line is given by

$$\frac{DM - QR}{RM} .$$

The equation of the line is therefore

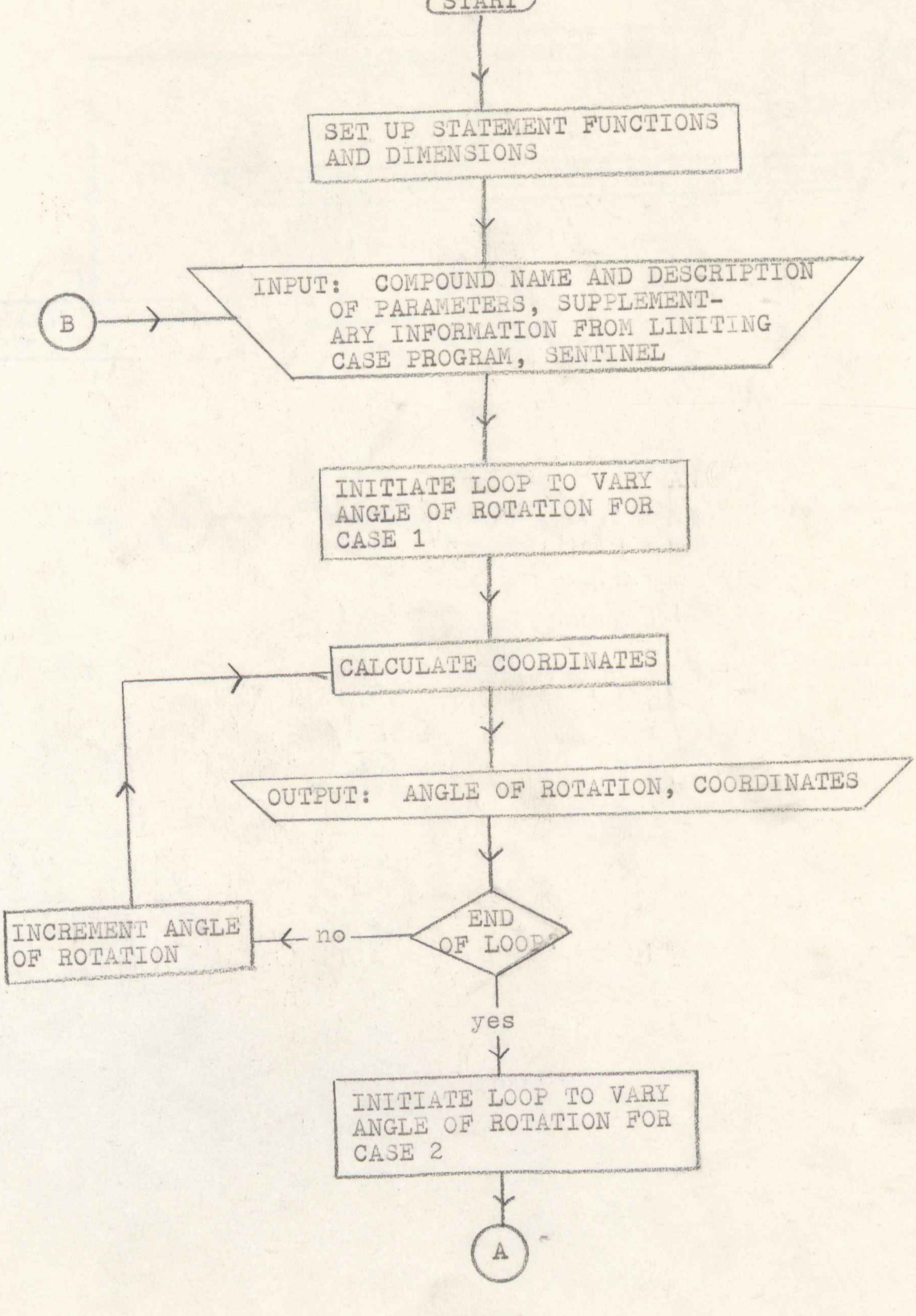
$$z = \frac{DM - QR}{RM}\, y' + z \text{ intercept}$$

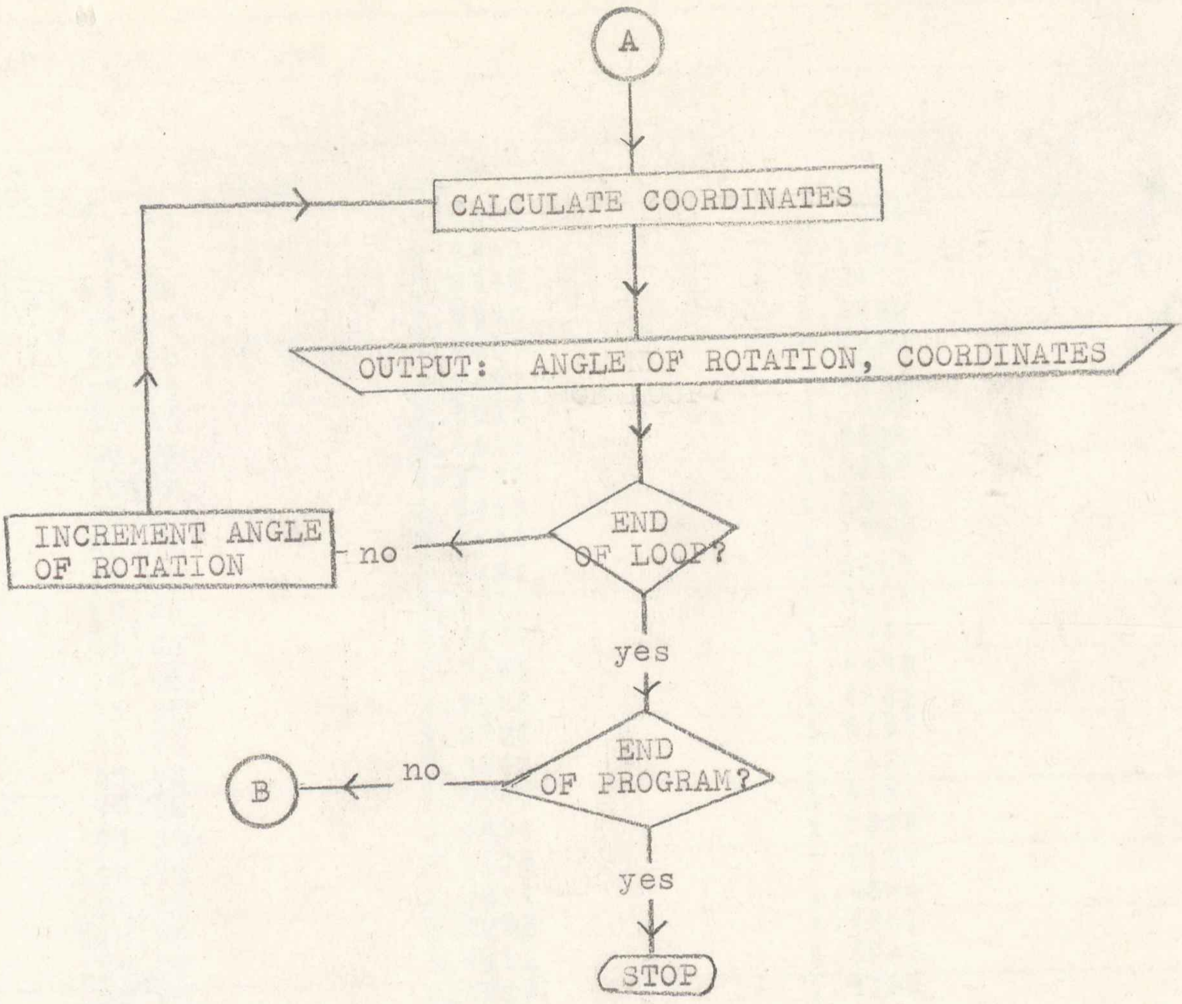
and the y' component is known from the determination of the rho coordinate. The z intercept, the point where the line crosses the z axis is point Q, a distance QR from the origin of the unprimed coordinate system. The equation for the projection becomes

$$z = \frac{DM - QR}{RM}\, y' + QR.$$

For the intermediate cases, the computer again played a large part. With this second program it was possible to set up a loop to take values of the angle of rotation from 0° to 180° in increments of 5° and calculate the rho and z coordinates for each. Appendix B is the listing of the actual program. Figures 22 and 23 are the flowchart and a sample of the computer output, respectively.

Figure 22. Flowchart of intermediate conformation program.




A
CALCULATE COORDINATES
OUTPUT: ANGLE OF ROTATION, COORDINATES
END OF LOOP?
no
INCREMENT ANGLE OF ROTATION
yes
END OF PROGRAM?
no
B
yes
STOP

```
DIPHENYLMETHANE  METHYLENE ANGLE +10 FROM INPUT DATA

TATIONARY RING IN PLANE


 ANGLE OF ROTATION          RHO                       Z
       0.00               2.5355                   0.0000
       5.00               2.5357                   0.1341
      10.00               2.5365                   0.2671
      15.00               2.5380                   0.3982
      20.00               2.5407                   0.5262
      25.00               2.5450                   0.6502
      30.00               2.5515                   0.7692
      35.00               2.5611                   0.8824
      40.00               2.5742                   0.9889
      45.00               2.5918                   1.0879
      50.00               2.6144                   1.1786
      55.00               2.6427                   1.2603
      60.00               2.6771                   1.3324
      65.00               2.7179                   1.3944
      70.00               2.7651                   1.4458
      75.00               2.8188                   1.4862
      80.00               2.8787                   1.5153
      85.00               2.9442                   1.5328
      90.00               3.0147                   1.5387
      95.00               3.0894                   1.5329
     100.00               3.1674                   1.5154
     105.00               3.2477                   1.4864
     110.00               3.3293                   1.4461
     115.00               3.4111                   1.3948
     120.00               3.4919                   1.3329
     125.00               3.5707                   1.2608
     130.00               3.6466                   1.1791
     135.00               3.7184                   1.0885
     140.00               3.7853                   0.9896
     145.00               3.8464                   0.8832
     150.00               3.9010                   0.7700
     155.00               3.9484                   0.6510
     160.00               3.9880                   0.5270
     165.00               4.0193                   0.3991
     170.00               4.0419                   0.2680
     175.00               4.0556                   0.1350
     180.00               4.0603                   0.0009
```

Figure 23. Sample of output from intermediate conformation program.

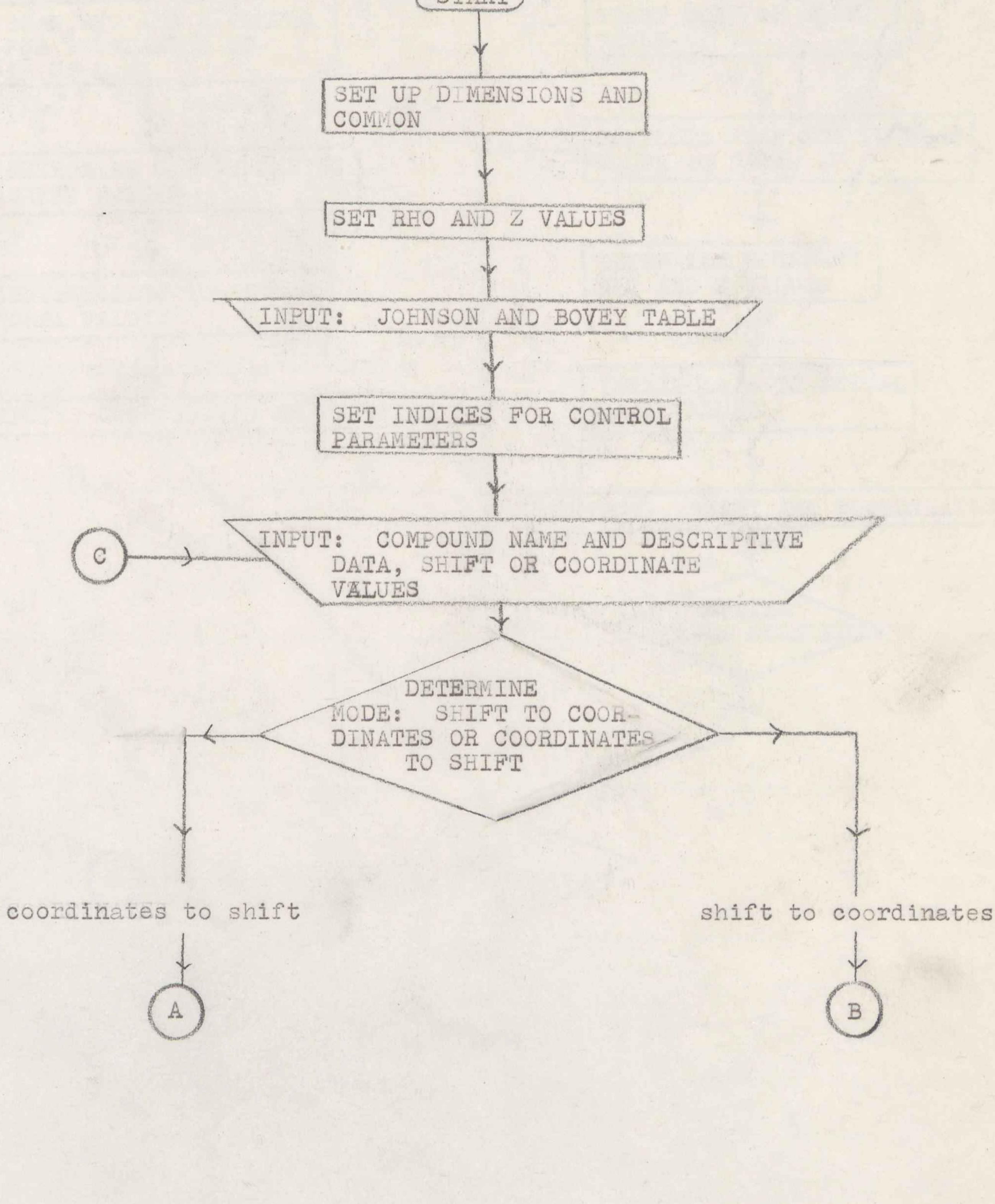
```
DIPHENYLMETHANE  METHYLENE ANGLE +10 FROM INPUT DATA

TATIONARY RING OUT OF PLANE


  ANGLE OF ROTATION          RHO                   Z
         0.00               1.6672               1.9103
         5.00               1.6733               1.9080
        10.00               1.6913               1.9013
        15.00               1.7213               1.8899
        20.00               1.7631               1.8736
        25.00               1.8165               1.8522
        30.00               1.8811               1.8253
        35.00               1.9568               1.7923
        40.00               2.0430               1.7528
        45.00               2.1393               1.7062
        50.00               2.2450               1.6521
        55.00               2.3591               1.5898
        60.00               2.4804               1.5191
        65.00               2.6074               1.4398
        70.00               2.7380               1.3523
        75.00               2.8702               1.2573
        80.00               3.0015               1.1561
        85.00               3.1292               1.0502
        90.00               3.2511               0.9420
        95.00               3.3652               0.8338
       100.00               3.4698               0.7280
       105.00               3.5641               0.6267
       110.00               3.6479               0.5317
       115.00               3.7211               0.4442
       120.00               3.7846               0.3650
       125.00               3.8389               0.2943
       130.00               3.8851               0.2320
       135.00               3.9240               0.1778
       140.00               3.9565               0.1312
       145.00               3.9835               0.0917
       150.00               4.0056               0.0588
       155.00               4.0233               0.0318
       160.00               4.0373               0.0104
       165.00               4.0477               -.0059
       170.00               4.0550               -.0173
       175.00               4.0593               -.0240
       180.00               4.0607               -.0263
TOP           0049
```

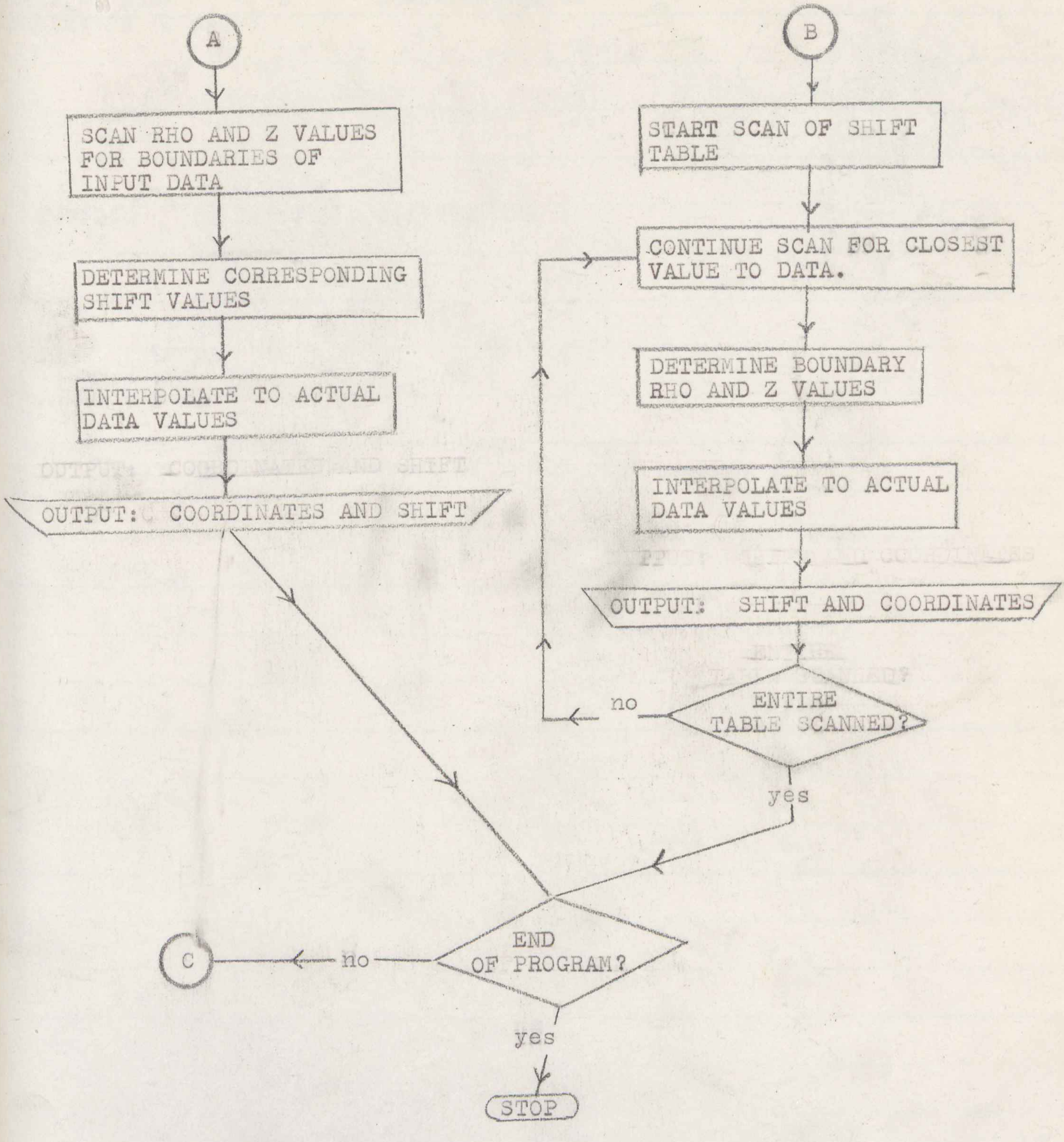
Figure 23. (contd.)

With all the coordinates calculated all that remains is to read the table of Johnson and Bovey, interpolate to the values determined and obtain the theoretical chemical shift. In this case too, the volume of data to be handled dictates further use of the computer. In addition, this program has been modified in such a way as to allow it to read in shift values and determine coordinates as well as vice versa. The purpose of this approach is that if NMR data are obtained for diphenylmethane or similar systems in which all internal rotation is stopped, these data can be matched to possible coordinates that will fit the experimental evidence. The same idea can be carried to the first two programs also. That is, the coordinate values can be used as input anf possible geometric structures can be determined. Thie did not permit the modification of the geometry programs.

A listing of this table-read program is given in Appendix C. Figures 24 and 25 are the flowchar and sample of output. The outout sample is for operation under the coordinate input-shift output mode.

Figure 24. Flowchart of table-read program.




A
SCAN RHO AND Z VALUES FOR BOUNDARIES OF INPUT DATA
DETERMINE CORRESPONDING SHIFT VALUES
INTERPOLATE TO ACTUAL DATA VALUES
OUTPUT: COORDINATES AND SHIFT
B
START SCAN OF SHIFT TABLE
CONTINUE SCAN FOR CLOSEST VALUE TO DATA.
DETERMINE BOUNDARY RHO AND Z VALUES
INTERPOLATE TO ACTUAL DATA VALUES
OUTPUT: SHIFT AND COORDINATES
ENTIRE TABLE SCANNED?
no
yes
END OF PROGRAM?
no
C
yes
STOP

```
IPHENYLMETHANE    - 10      COPERPANDICULAR
COORDINATES TO SHIFT


      RHO             Z              SHIFT


  2.93200       1.14610       0.19953
```

Figure 25. Sample output of table-read program .

rho	z 0.00	0.10
.000	-15.24785	-15.19186
.100	-15.22949	-15.20813
.200	-15.25697	-15.25100
.300	-15.27543	-15.30041
.400	-15.23423	-15.31473
.500	-15.04181	-15.21565
.600	-14.54548	-14.86221
.700	-13.52070	-14.01601
.800	-11.71793	-12.33471
.900	-9.04120	-9.53817
.000	-5.80966	-5.88930
.100	-2.74135	-2.42407
.200	-.46070	-.03960
.300	0.89236	1.21637
.400	1.53350	1.72902
.500	1.74367	1.84663
.600	1.73014	1.77894
.700	1.61538	1.63546
.800	1.46392	1.46965
.900	1.30723	1.30620
.000	1.15941	1.15548
.100	1.02586	1.02095
.200	0.90784	0.90285
.300	0.80468	0.80002
.400	0.71497	0.71079
.500	0.63709	0.63343
.600	0.56945	0.56627
.700	0.50161	0.50787
.800	0.45930	0.45694
.900	0.41443	0.41241
.000	0.37508	0.37334
.100	0.34045	0.33895
.200	0.30988	0.30858
.300	0.28281	0.28169
.400	0.25876	0.25779
.500	0.23734	0.23649
.600	0.21819	0.21745
.700	0.20103	0.20039
.800	0.18562	0.18505
.900	0.17173	0.17123
.000	0.15919	0.15874

Figure 25. contd. Segment of table scanned.

Apparatus:

All spectra were taken on a Varian A-60 Nuclear Magnetic Resonance Spectrometer with a variable temperature probe. The probe allows studies to be made in a range of -100° to $+ 200^\circ$ C.

In this particular study the lower temparature range, $- 100^\circ$ to $+ 40^\circ$, was used. The magnet is designed to allow gas to circulate through the sample area. A dewer of liquid nitrogen can be mounted on the outside of the magnet housing. To cool the sample, gaseous nitrogen is pumped through the liquid nitrogen and circulated through the magnet. Temperature control can be programmed by a thermistor in the control box of the probe. (Figure 26).

A more accurate indication of temperature can be obtained by inserting a methanol sample into the probe and scanning its spectrum. The spectrum shows two peaks, one from the methyl protons and one from the hydroxy proton. The separation of these peaks is directly related to the temperature of the sample. Figure 27 shows a plot of this relationship.

Reagents used in NMR spectra:

Diphenylmethane	Eastman Organic Chemicals (practical grade)
Dichlorodiphenylmethane	Aldrich Chemical Co. (N_D^{20} 1.6040)

Reagents selected for potential use:

p (2-phenyl-iso-propyl) phenol	Eastman Organic Chemicals
4,4' Methylenebis(2,6 di-tert-butylphenol)	"
Bis (2,4 dinitrophenyl) methane	"
α,α Dibromodiphenylmethane	synthesized by Dr. William B. Martin, Union College

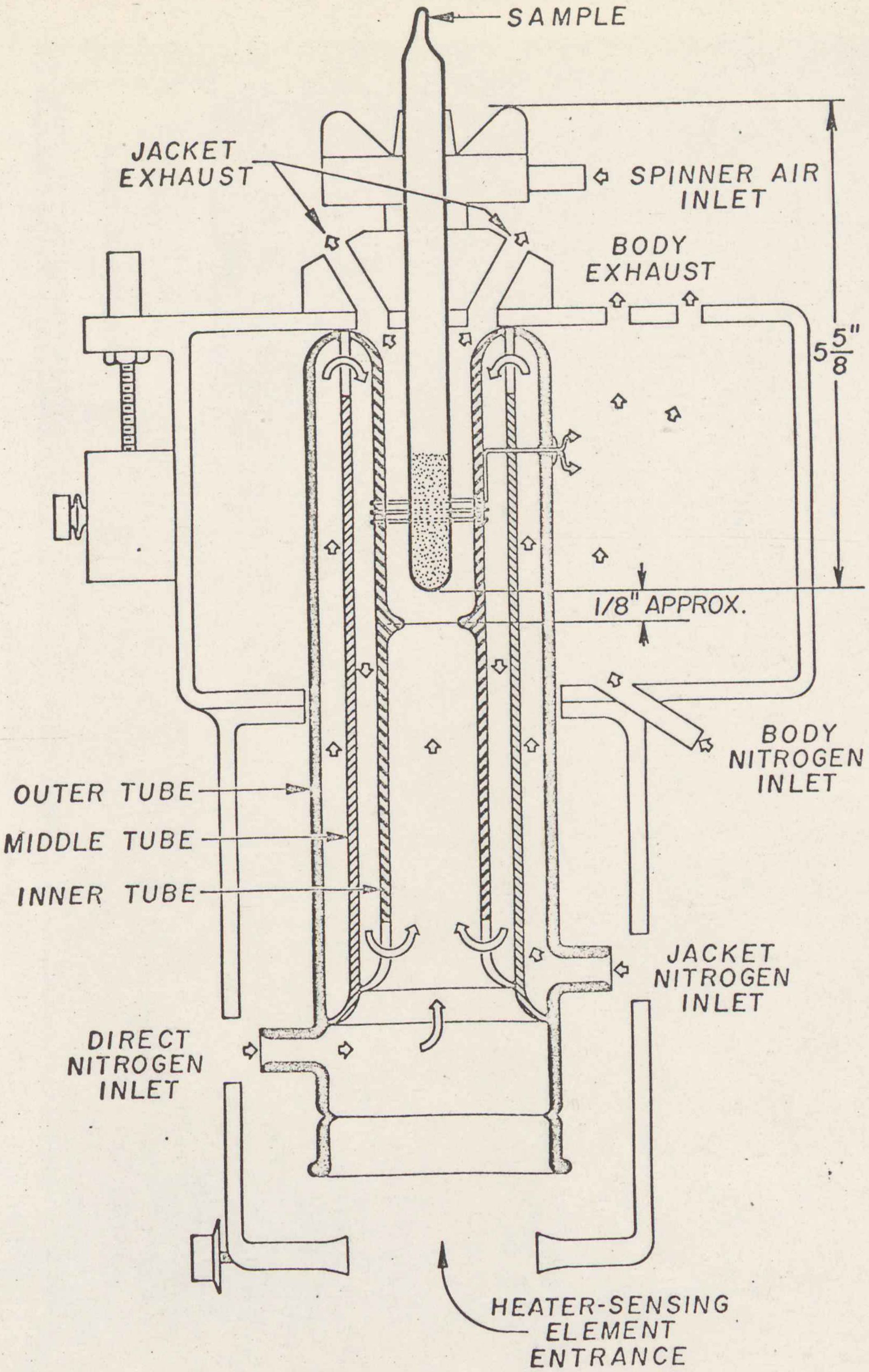
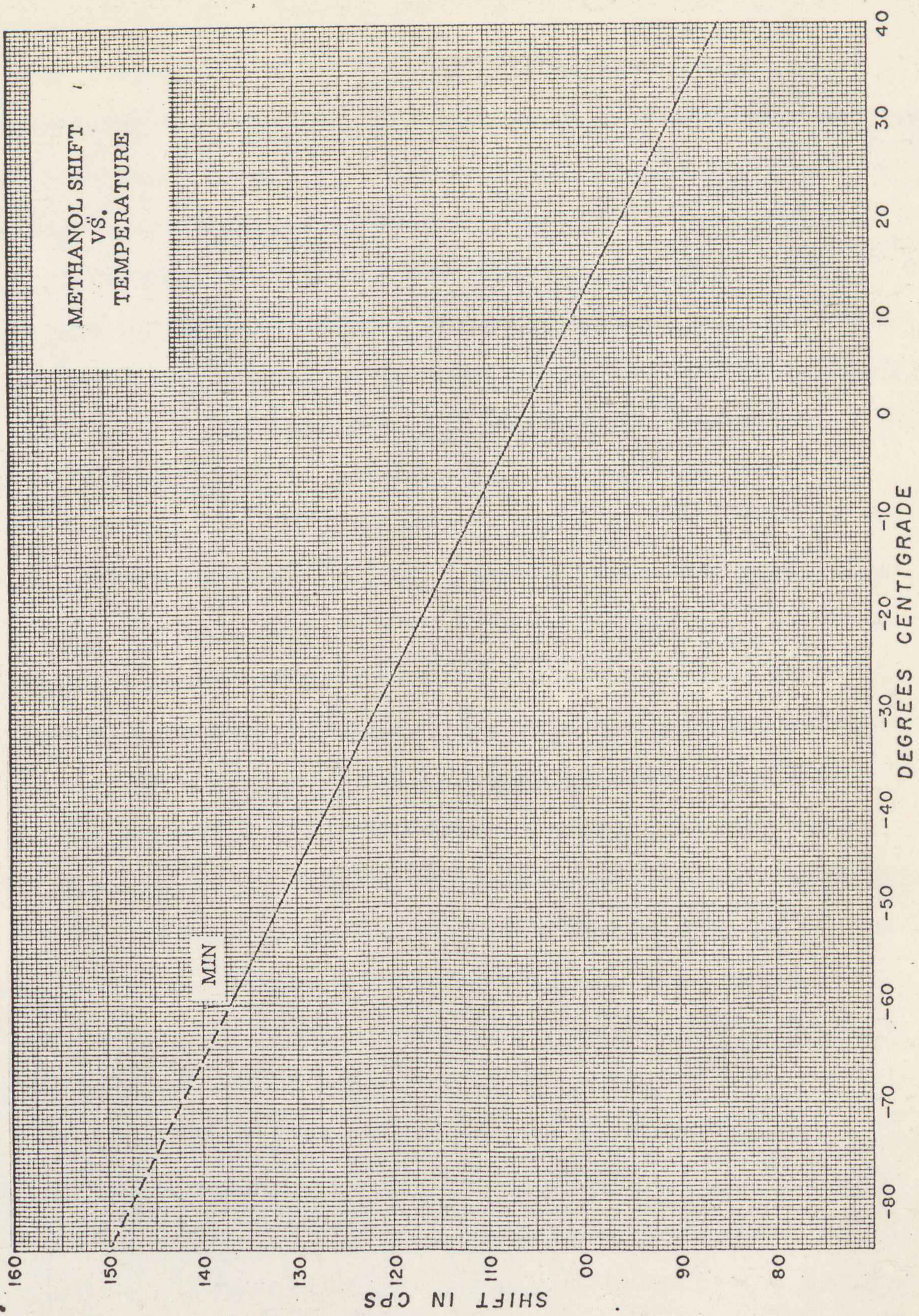


Figure 26. Schematic representation of the Varian Variable Temperature Probe (6).

Figure 27. Methanol shift vs. temperature (6).



Experimental Results:

With a resonably solid theoretical foundation the problem of determining the lowest energy conformation of a diphenylmethane system becomes experimental. Due to the lack of time, only preliminary work could be done on this aspect of the problem. With this in mind, some techniques were explored in hopes of finding one or two that might prove a reasonable approach. The possibilities can be divided into three categories: 1) studies on solutions of diphenylmethane and derivatives, 2) studies on the neat compound, and 3) studies using absorbents.

1) Studies on solutions of diphenylmethane and derivatives.

The original approach to the experimental part of the study was to dissolve the sample in a suitable solvent, reduce the temperature and scan spectrum. The expectation was that the low temperature would remove enough energy from the system to keep the rings from rotating as they do under normal conditions. By use of a solvent as opposed to a neat sample, the system would hopefully remain a liquid and therefore not allow the spin-spin relaxation phenomenon, previously mentioned, to occur. The aromatic peak that is a singlet at room temperature (Figure 5) was expected to show some form of splitting under the new conditions.

The procedure was first attempted for diphenylmethane itself using $CDCl_3$ as a solvent. The spectrum run at - 50° showed no apparent change from that at room temperature, nor did the one at - 65°. At temperatures lower than - 65° the solution began to solidfy. This was characterized by a general broadening and flattening of all the peaks in the spectrum, including the internal reference TMS. This broadening was an intermediate stage. Ultimately the entire spectrum disappeared when the sample became completely solid.

To give lower temperature capabilities the solvent was changed. Spectra were taken as low as - 70° in CS_2, acetone, diethyl ether and n-hexane. The main reasons for these solvents were that they were all low melting (CS_2: - 112°; acetone: - 95°; diethyl ether: - 116°; n-hexane: - 95°) and their NMR spectrum did not interfere or overlap with that of diphenylmethane. Still at - 70° no change from the room temperature aromatic absorption could be observed. Attempts were made to go to even lower temperatures, but these were not successful due to the solidifying of the solution. Besides variation of the solvent, some variation of concentration was also attempted in each solvent. This too proved to be of no experimental value.

The same approach was repeated, this time using solutions of α,α dichlorodipenylmethane. (Figure 28).
In this system there is a greater possibility for steric effects to stop the rotation. The chlorine atoms being more bulky than the hydrogens in diphenylmethane might block or slow rotation to such an extent that temperatures above the freezing point of the solution might sufficiently remove energy from the molecule to stop rotation. Experimental results, however, indicate that such is not the case.

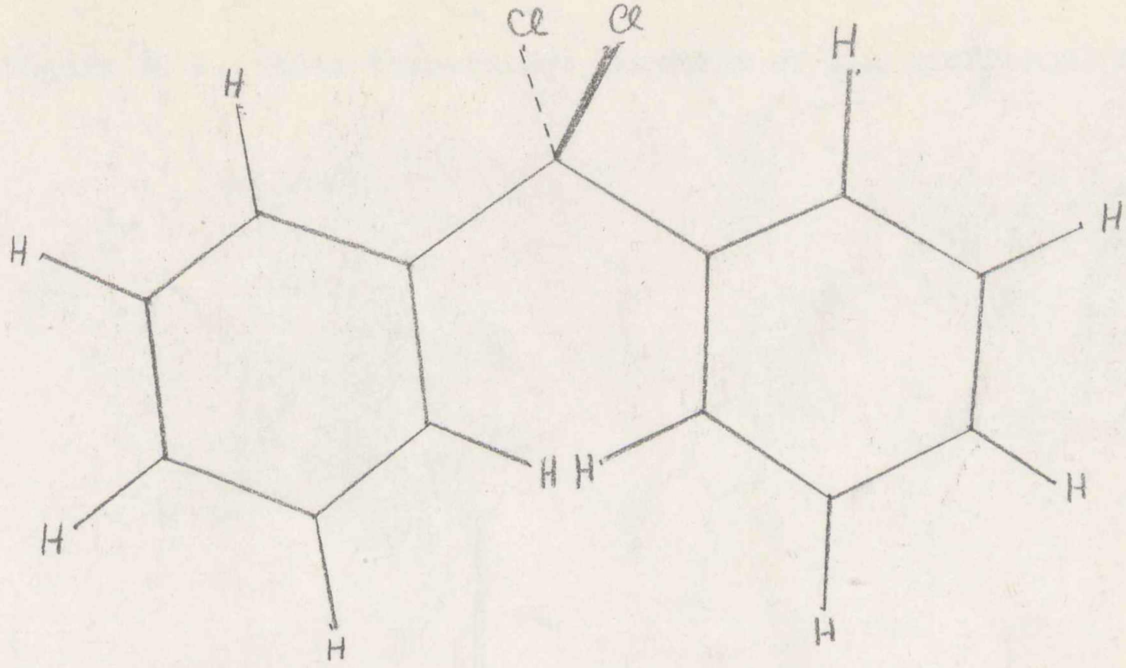


Figure 28. Dichlorodiphenylmethane.

Figure 29, a and b, gives some indication of how a spectrum is affected as solid begins to form in the sample. Spectrum a is a room temperature spectrum of α,α dichlorodiphenylmethane and b is the same sample at - 60°. Spectrum b is in the range between the completely solid and the completely liquid states. It is probably more in the liquid area. Were the sample a complete solid, no spectrum at all would be visible.

Future studies of the problem using this approach might assume a more quantitative aspect. The first suggestion is that thermal studies be carried out in various solvents to determine 1) the solvent capable of achieving the lowest temperatures before solidifying and 2) the optimum concentration of the derivative in this solvent. In the first area, the solvent must meet the requirements of low freezing point and no interference with the spectrum of the compound being studied. The

Figure 29 a. Room temperature spectrum of α,α dichlorodiphenylmethane.

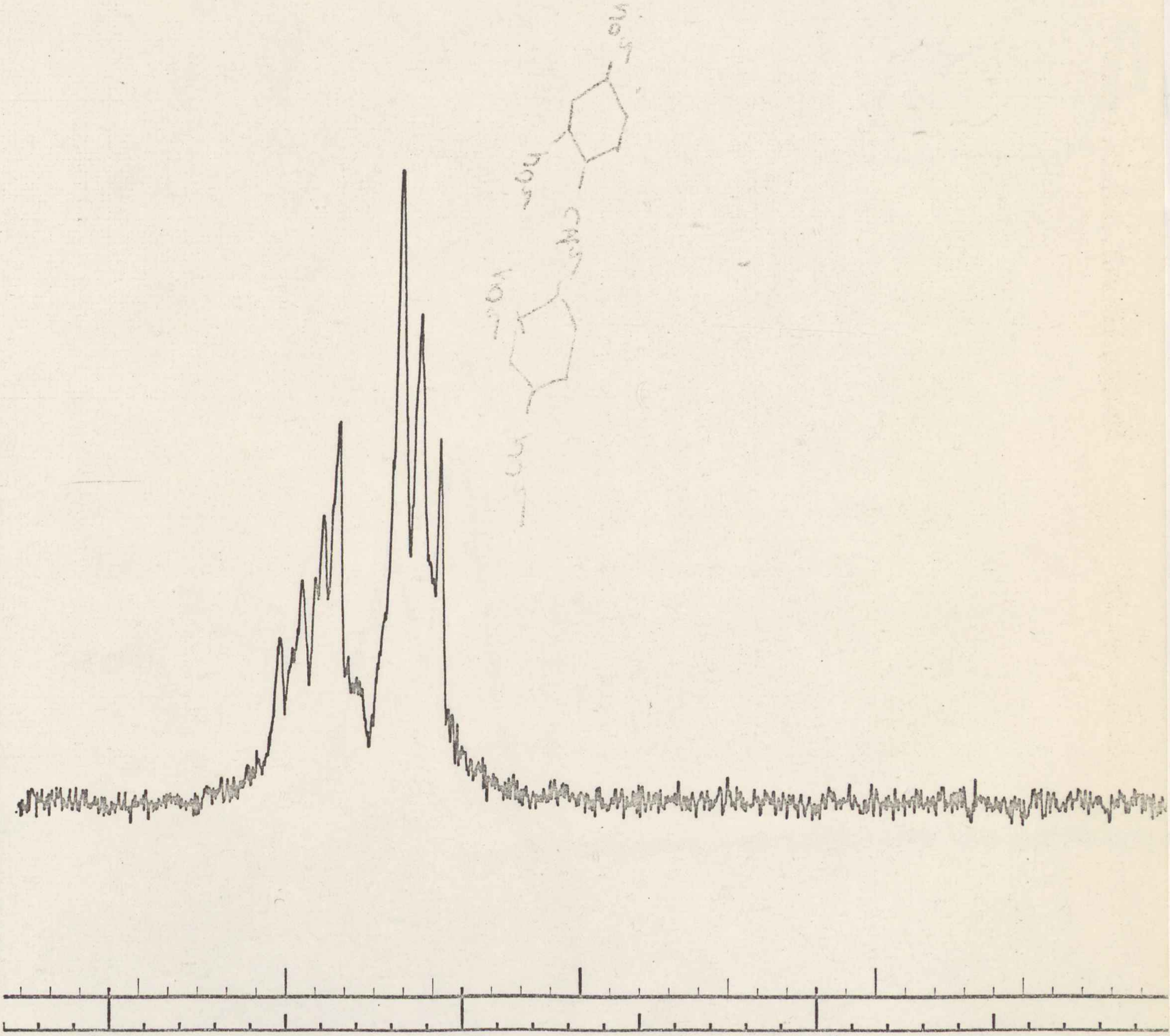
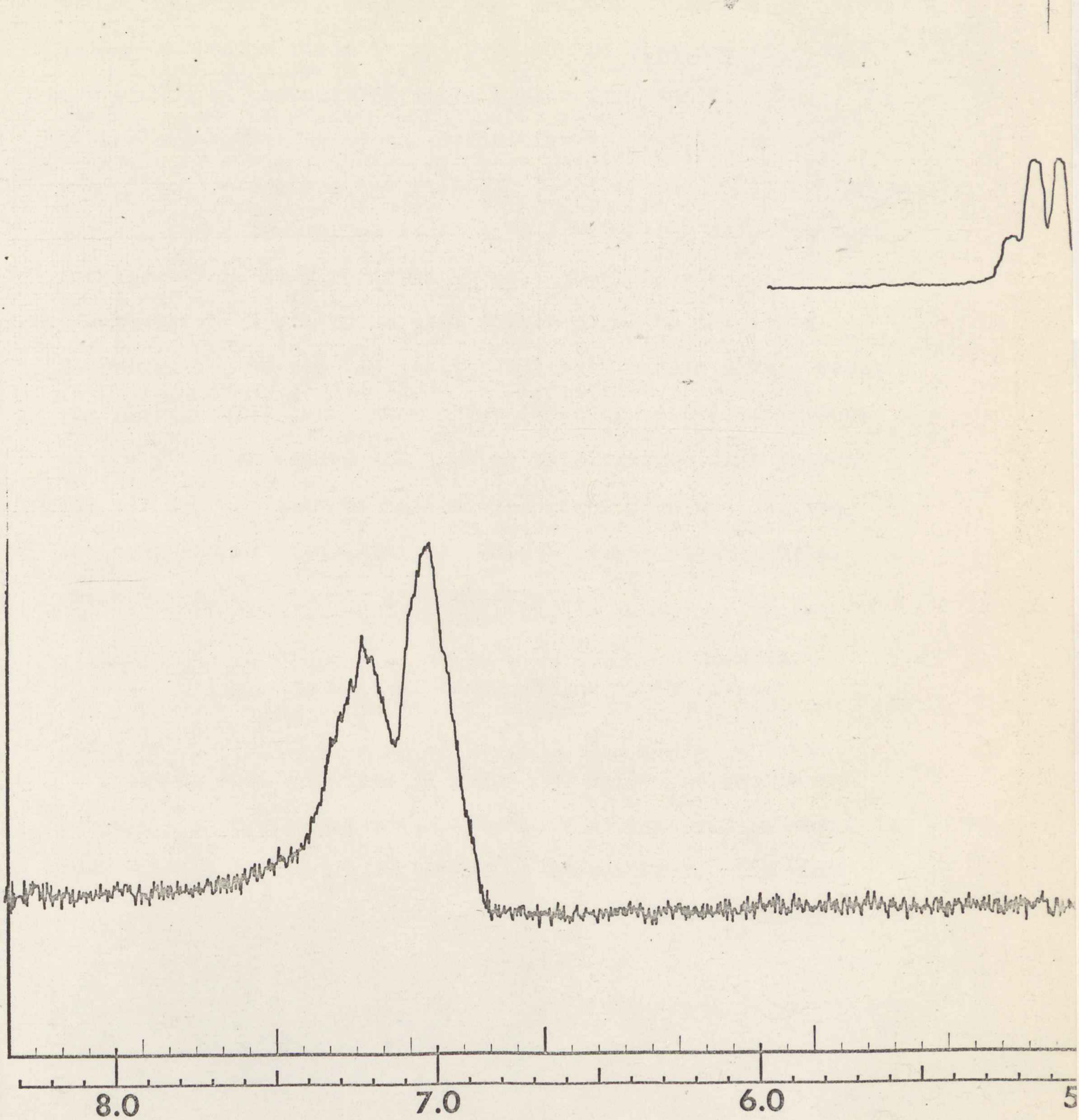


Figure 29 b. Spectrum of dichlorodiphenylmethane at - 60° C.



second consideration requires that the concentration be large enough so that a readable spectrum can be obtained and yet low enough to prevent the whole system from solidifying. If the concentration of the derivative is high it can have the effect of raising the freezing point of the solid substantially. Too high a concentration could give a resulting solution that freezes before ring rotation stops. Should these studies prove unsuccessful, a binary solvent system might be developed. A combination of two low melting solvents should give a resulting mixture that has a much lower freezing point than either of the two pure components. Using this mixture as a solvent for the diphenylmethane derivatives might give the desired low temperature capabilities. Such a system might suffice where the pure solvents are inadequate.

2) Studies on neat diphenylmethane derivatives.

The region, referred to above, in which the sample is between the liquid and solid states is of interest in examining neat samples of the diphenylmethane derivatives. The neat samples give two advantages over solutions in this intermediate state. The first is that this state occurs at a much higher temperature. There is not the amount of instrument instability which exists when the probe is in the - 50 to - 70° range. Secondly, with the neat sample the possibility that any stopping of rotation will be an intermolecular, rather than an intramolecular, phenomenon is lessened. The presence of a solvent makes it necessary to determine what effect, if any, solvent molecules have on hindering the ring rotation.

Figure 30 shows a series of spectra over a range of temperatures. The area shown is the aromatic region of the diphenylmethane spectrum. For this series, the sample was cooled to 0° C. and the temperature slowly increased with the spectrum scanned at 2 degree intervals. The bottom spectrum, 0°, is where the sample is almost entirely solid. It remains this way up to about 12°. In the spectrum at this point the very faint beginnings of the aromatic peak can be seen. This peak grows progressively larger until it ultimately gives the spectrum of the liquid at 28°.

Unfortunately time did not allow detailed study of this method. It is suspected that the temperature range between 12° and 24° might yield some interesting results. In this area the crystal forces might be strong enough to lock the rings into a fixed orientation, but not so strong that they allow spin-spin relaxation to occur to too great an extent.

3) Studies on diphenylmethane derivatives with adsorbents.

A third method attempting to restrict internal ring rotation was the addition of an adsorbent to the sample. The procedure was to add a small amount of a known adsorbing material to a neat sample of the compound being studied. It was hoped that one of two processes would take place. If the molecule attached itself to the adsorbing particle, the particle might

~~Figure 26.~~ Figure 30 Series of spectra from the aromatic region of diphenylmethane spectrum from 0° to 28°.

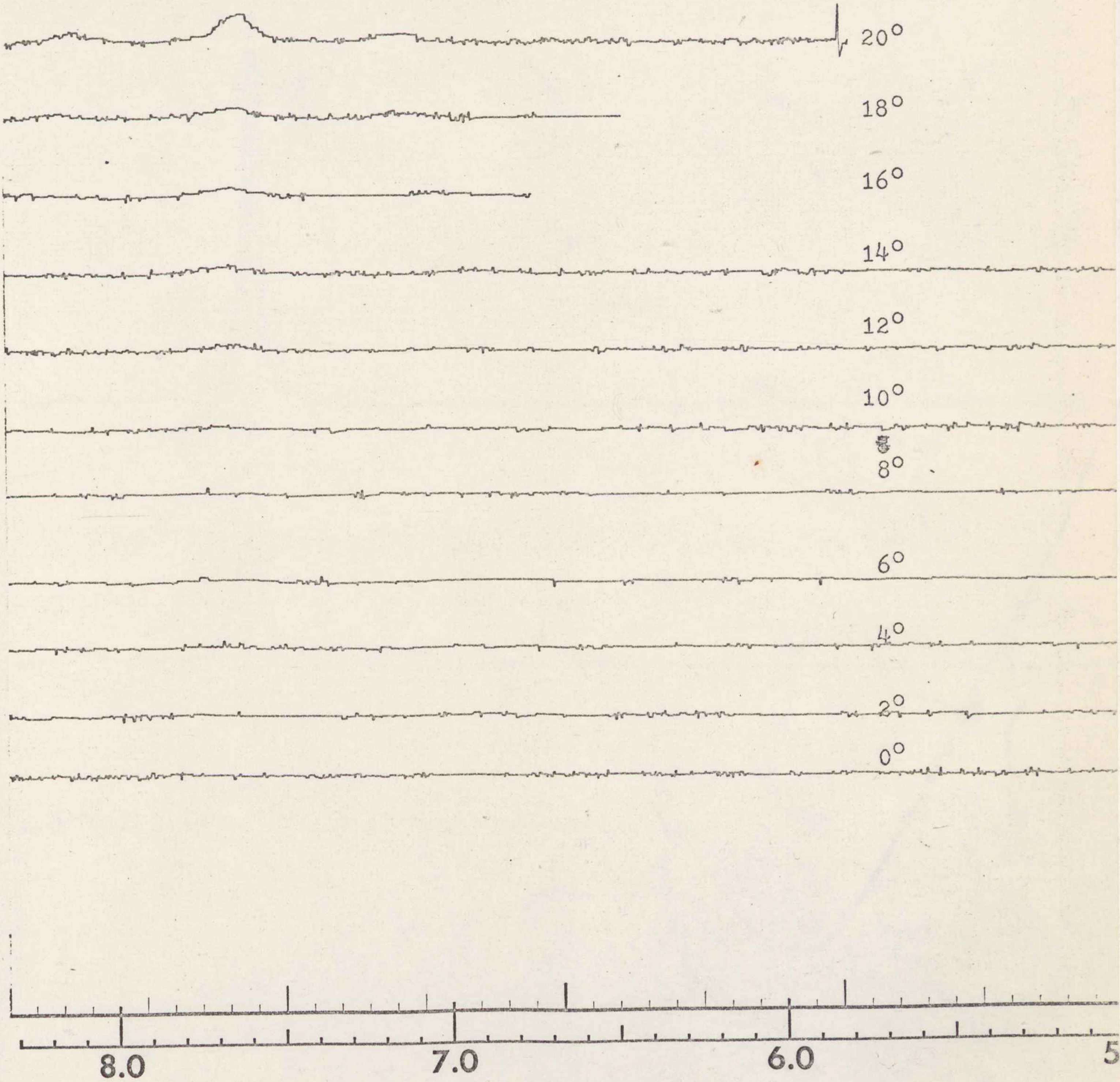


Figure 30. cont

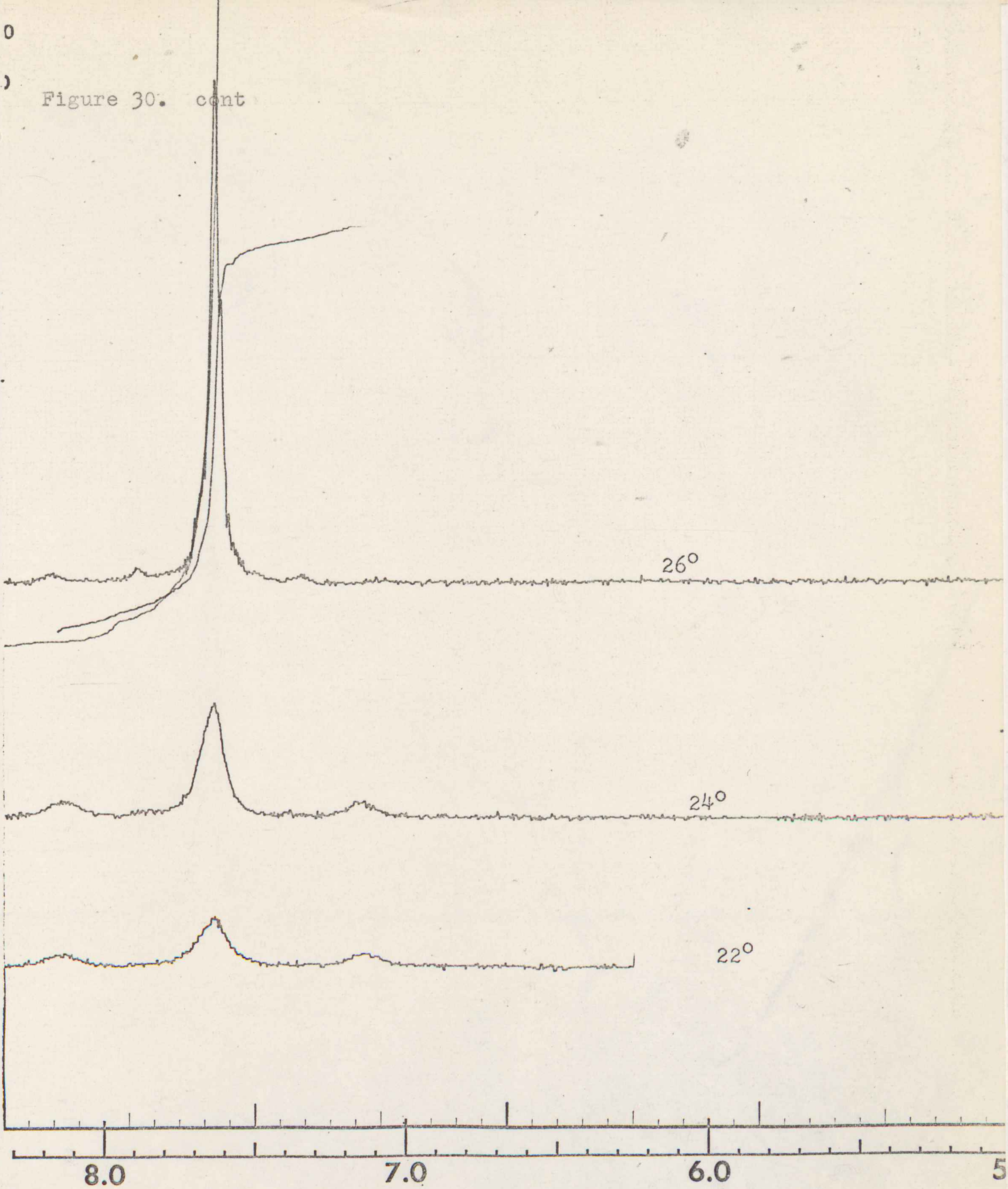
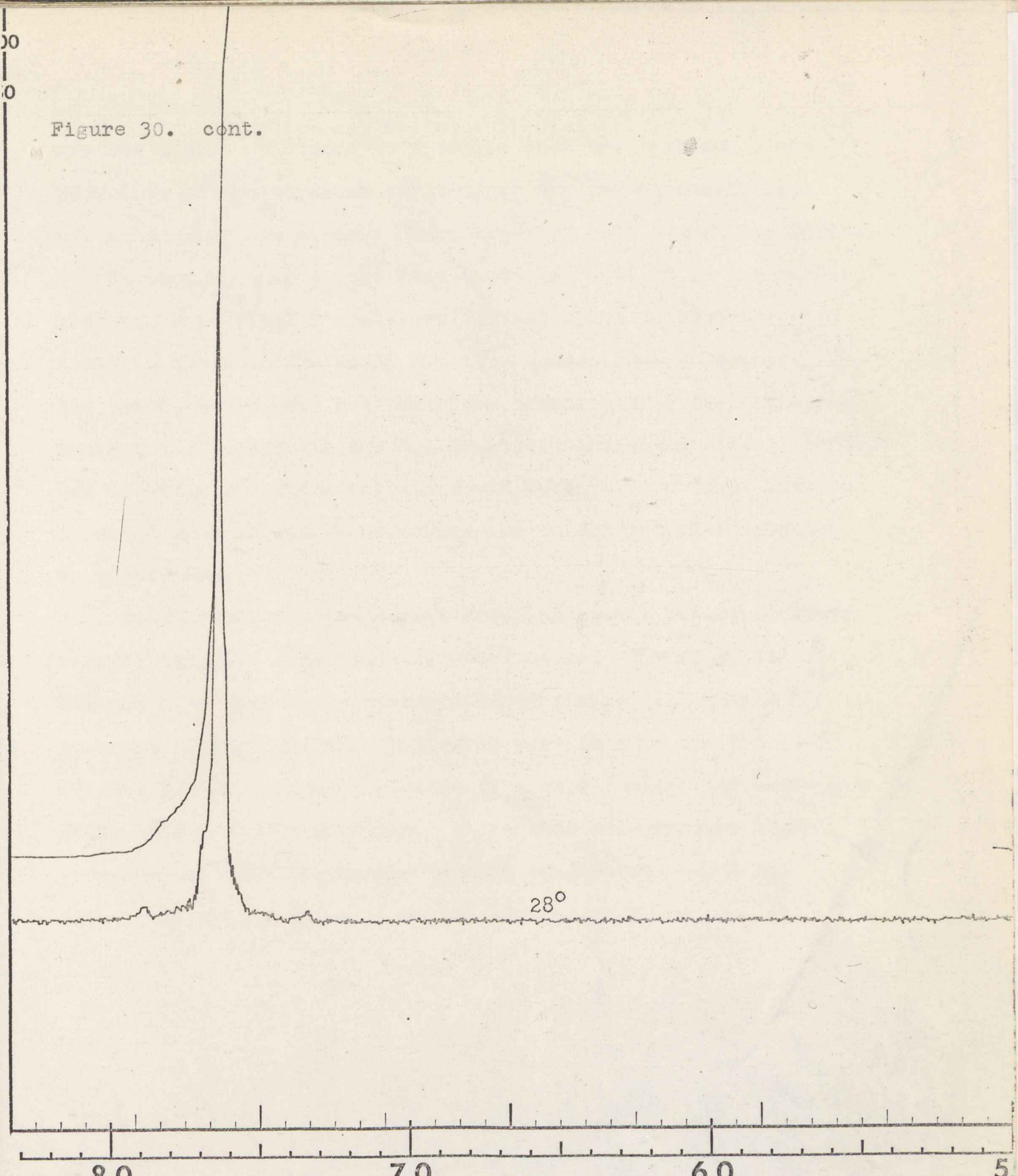


Figure 30. cont.



provide enough hindrance to rotation that the spectrum might show some of the expected splitting. The second possibility has to do with the powdery consistency of most common adsorbents. It was thought that as the fine particles settled in the sample they might physically occupy sufficient space so that the rings in the molecule would not have enough room to rotate. The sample would have a slurry-like consistency. The diphenylmethane derivative would still be liquid and hence give a readable NMR spectrum and the adsorbent would be forming a "semi lattice" in which trapped sample molecules are so crowded that rotation is impossible.

Again, time did not permit detailed study, but preliminary results indicate that splitting will occur. Figure 31 is the aromatic peak of a diphenylmethane sample with animal charcoal added. The one difficulty here is that the TMS peak (Figure 32) of the same spectrum is also distorted and seemingly split into a number of parts. It is this complication that prevents one from making any general conclusions about the rotational structure based on the adsorption procedure.

Figure 31. Aromatic region of diphenylmethane-bone-black spectrum.

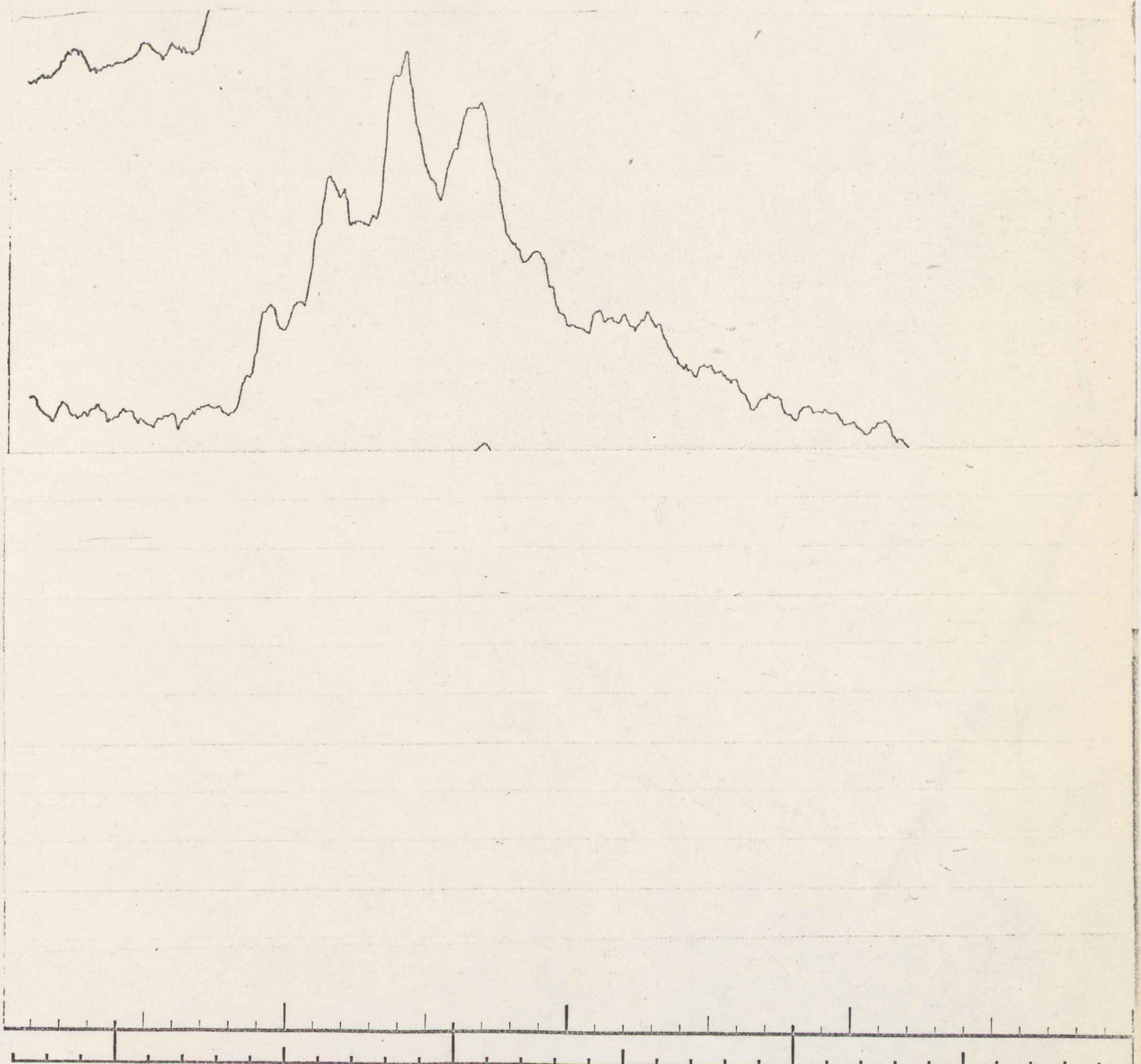
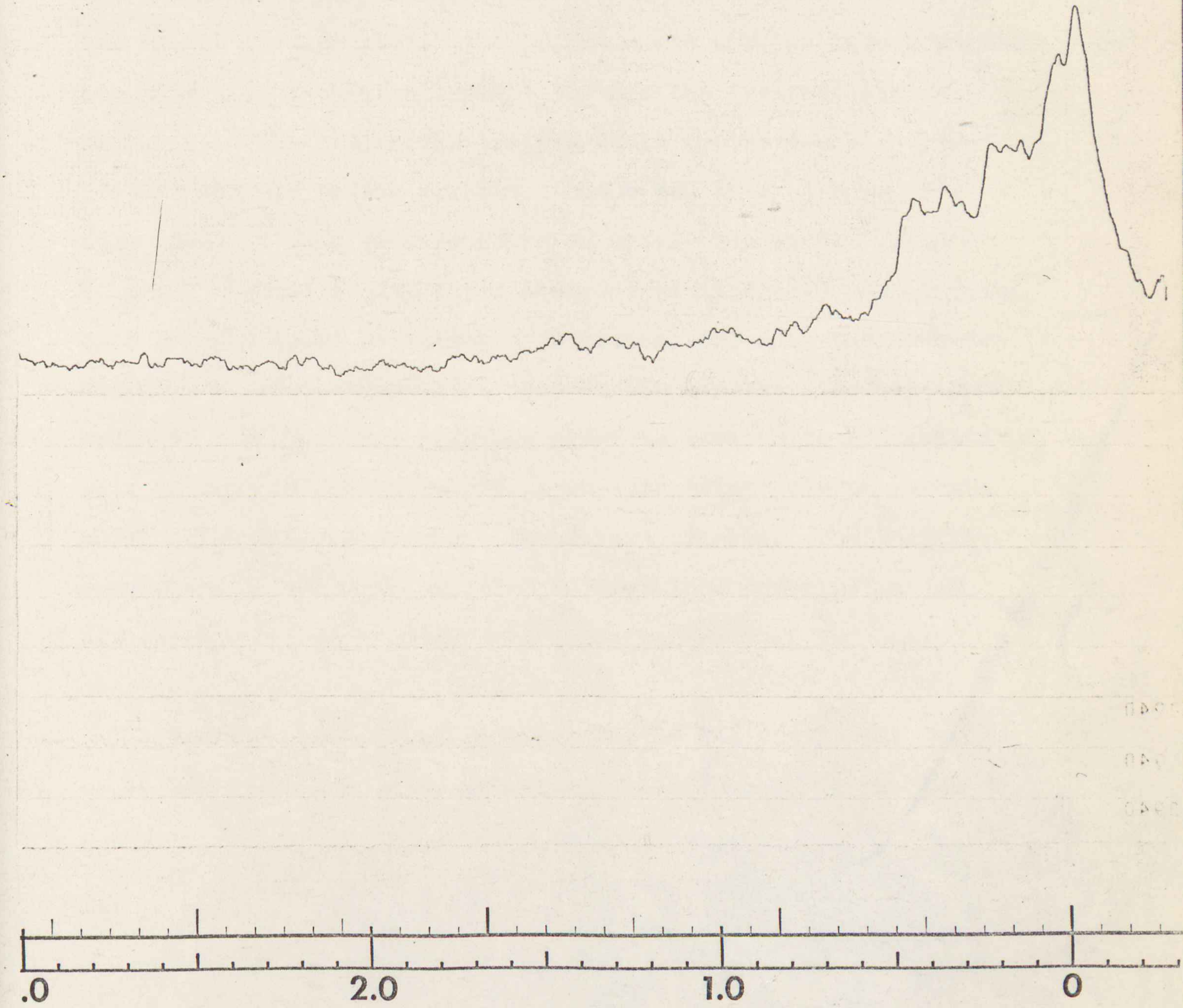


Figure 32. TMS peak of diphenylmethane-bone-black spectrum.



Suggestions for further work:

Some possible approaches to continuing this study have already been mentioned in conjunction with the preliminary experiments. There is also some work to be done in finalizing the use of the computer. The programs are not, as they now stand, in their most versatile state. Perhaps the greatest single addition to the table-read program would be the use of a peripheral storage device for the Johnson and Bovey table. For this either a tape or disc could be used. The latter would be ideal because of its rapid access capabilities. The limiting case program could be expanded to account for more than the two simple sets of intermediates that it now handles. As mentioned earlier, both geometry programs might be revised to accomodate both coordinate and geometric input data being able to operate under two modes, as does the table-read program. The geometry programs might also be modified to calculate coordinates for all the protons on a given derivative rather than for the one ortho proton, as it now does.

Once these additions are implemented the final step would be to interface all three programs. Under such a system one would be able to do both of the following:

1) input: compound description and bond length and angle data

output: coordinates and shifts for all protons in all conformations

2) input: chemical shift data experimentally determined

output: possible rotational isomers responsible for the shift data.

Footnotes

(1) Robert M. Silverstein and G. Clayton Bassler, Spectrometric Identification of Organic Compounds, second edition, John Wiley & Sons, Inc., New York, 1967, p. 116.

(2) Ibid., p. 117.

(3) C. E. Johnson, Jr. and F. A. Bovey, J. Chem. Phys. 29, (1958), p. 1012.

(4) J. W. Ensley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Volume 1, Pergammon Press, New York, 1965, Appendix B.

(5) The Chemical Society, Tables of Interatomic Distances and Configuration in Molecules and Ions, Burlington House, London, 1958.

(6) Varian A-60 Manual.

APPENDIX A

Listing of Limiting Case Geometry Program

```
$       TITLE   PAT COMI    RESEARCH:  GEOMETRY, LIMITING CASES
C  ORTHO HYDROGEN DISTANCES FROM CENTER (RHO) AND ABOVE PLANE (Z) OF OPPOSITE
C     RING IN DIPHENYL METHANE-LIKE SYSTEMS FOR THREE POSSIBLE CONFORMATIONS
      REAL HYPOT
      INTEGER NAME(50)
      RADIAN(ANGLE) = ANGLE*0.01745
      DEGREE(ANGLE) = ANGLE/0.01745
      HYPOT(X,Y) = SQRT(X**2 + Y**2)
C  IF A VARIABLE HAS X FOR ITS FIRST LETTER IT DENOTES A LENGTH,  IF THE
C     FIRST LETTERS ARE ANG THE VARIABLE DENOTES AN ANGLE
C  LETTER DESIGNATIONS
C          A-- METHYLENE CARBON
C         B -- CARBON ATOM ON RING I BONDED TO METHYLENECARBON
C         C--RINGI ORTHO CARBON
C         D--RING I ORTHO HYDROGEN
C         E-- CARBON ATOM ON RING II BONDED TO METHYLENE CARBON
C         G + F -- ORTHO CARBONS ON RING II
C         FP(F')-- META CARBON ON RING II
C         I -- CENTER OF RING II
 1000 READ(50,65) NAME
   65 FORMAT (50A1)
C   INPUT:
C       CARD1 COMPOUND NAME
C       CARD 2 BOND LENGTHS
C       CARD 3 BOND ANGLES
C       CARD 4 SENTINEL ( 1 OR 0   0 ONLY IF LAST SET OF DATA)
      READ(50,10) XAB,XBC,XCD,XAE,XEF,XFFP,
     1  ANGBAE,ANGABC,ANGBCD,ANGFEG
   10 FORMAT(6F10.4/4F10.4)
C   SET UP PARAMETERS TO VARY ANGLE BAE + OR - 10 DEGREES FROM INPUT VALUE
      ANGBAE = ANGBAE - 15.
      DO 808 IIII = 1,5
C   I AND K ARE INDEXING PARAMETERS USED IN THE OUTPUT SEGMENTS
      I = 0
      K = 0
      ANGBAE = ANGBAE + 5.
C  CALCULATION OF DISTANCES FOR COPLANAR CONFORMER
C  LENGTH AC     METHYLENE CARBON TO ORTHO CARBON ON RING I
C              CONSTRUCT TRIANGLE AJB:ANGLE AJB IS A RIGHT ANGLE
      ANGJBA = 180. - ANGABC
      ANGJBA = RADIAN(ANGJBA)
      CALL TRIG (XJA,XJB,XAB,ANGJBA)
      XJC = XJB +XBC
      XAC = HYPOT(XJA,XJC)
C  AC DETERMINED
C
C
C  LENGTH AD     METHYLENE CARBON TO ORTHO HYDROGEN ON RING I
C              CONSTRUCT TRIANGLE AKD: ANGLE AKD IS A RIGHT ANGLE
      ANGBCA = ATAN(XJA/XJC)
      ANGBCD = RADIAN(ANGBCD)
      ANGACD= ANGBCD - ANGBCA
      CALL TRIG(XDK,XCK,XCD,ANGACD)
      XAK = XAC-XCK
      XAD = HYPOT(XAK,XDK)
```

```
C  AD DETERMINED
C
C
C  LENGTH AI    METHYLENE CARBON TO CENTER OF RING II
C            DRAW GF INTERSECTING AI AT H PERPANDICULARLY
      ANGFEH = ANGFEG/2.
      ANGFEH = RADIAN(ANGFEH)
      XEH = XEF*COS(ANGFEH)
      XHI = XFFP/2.
      XAI = XAE + XEH + XHI
      ANGFEG = RADIAN(ANGFEG)
C  AI DETERMINED
C
C
C  ANGLE DAE    ORTHO HYDROGEN ON RING I TO METHYLENE CARBON ON RINGII BONDED
C          TO METHYLENE CARBON (SAME LINE AS TO CENTER OF RING II
      ANGCAD= ATAN(XDK/XAK)
      ANGBCA = DEGREE(ANGBCA)
      ANGBAC = 180.-ANGBCA -ANGABC
      ANGBAC = RADIAN(ANGBAC)
      ANGABC = RADIAN(ANGABC)
      ANGBAE = RADIAN (ANGBAE)
      ANGDAE = ANGBAE -ANGBAC - ANGCAD
C  DAE DETERMINED
C
C
C  LENGTH DI    ORTHO HYDROGEN ON RING I TO CENTER OF RING II (RHO)
C           CONSTRUCT TRIANGLE ILD; ANGLE ILD IS A RIGHT ANGLE
      CALL TRIG(XIL,XAL,XAI,ANGDAE)
      XDL = XAD-XAL
      XDI = HYPOT(XIL,XDL)
C  DI DETERMINED (RHO)
C
C
      RHO = XDI
C  Z = 0 -- BOTH RINGS ARE IN THE SAME PLANE
      Z = 0
C   OUTPUT:   HEADINGS AND KNOWN VALUES
      WRITE(66,99) NAME
   99 FORMAT(1H1, 50A1///)
      WRITE(66,101)
  101 FORMAT (10X,12HKNOWN VALUES///)
      WRITE(66,102) XAB,ANGBAE,XBC,ANGABC,XCD,ANGBCD,XAE,ANGFEG,XEF,XFFP
  102 FORMAT(20X,4HXAB=,F6.4,20X,7HANGBAE=,F6.4//20X,4HXBC=,F6.4,20X,
     17HANGABC=,F6.4// 20X,4HXCD=,F6.4,20X,7HANGBCD=,F6.4//20X,4HXAE=,
     2F6.4,20X,7HANGFEG=,F6.4//20X,4HXEF=,F6.4//20X,5HXFFP=,F6.4//////
     3/////)
      WRITE(66,103)
  103 FORMAT(10X,12HCONFORMATION,20X,3HRHO,20X,1HZ///)
C RETURN ALL KNOWN ANGLES TO DEGREES
      ANGBAE = DEGREE(ANGBAE)
      ANGABC = DEGREE(ANGABC)
      ANGFEG = DEGREE(ANGFEG)
      ANGBCD = DEGREE(ANGBCD)
      GO TO 800
```

```
C CALCULATION FOR PLANAR-PERPANDICULAR CONFORMER
C  THE ORTHO HYDROGEN DOES NOT CHANGE POSITION WITH RESPECT TO THE METHYLENE
C           CARBON
C              CONSTRUCT TRIANGLE AMD : ANGLE AMD IS A RIGHT ANGLE
  801 CALL TRIG(XDM,XAM,XAD,ANGDAE)
      XIM = XAI - XAM
      RHO = XIM
      Z = XDM
      GO TO 800
C  CALCULATION  FOR COPERPANDICULAR CONFORMATION
  802 ANGBAD= ANGBAC+ ANGCAD
C              CONSTRUCT TRIANGLE AQD  : ANGLE AQD IS A RIGHT ANGLE
      CALL TRIG(XDQ,XAQ,XAD,ANGBAD)
C             CONSTRUCT RECTANGLE DQRS PERPANDICULAR TO THE PLANE OF RING II
      ANGRAQ = 180. - ANGBAE
      ANGRAQ = RADIAN(ANGRAQ)
      CALL TRIG (XQR,XAR,XAQ,ANGRAQ)
      Z = XQR
      XRS = XDQ
      XIR = XAR + XAI
      XSI = HYPOT(XAR + XAI,XRS)
      RHO = XSI
      GO TO 800
C   OUTPUT    RHO AND Z COORDINATES
C   SUPPLEMENT IS FOR FUTURE PROGRAMS
  800 I = I + 1
      RHO = RHO/1,3900
      Z = Z/1,3900
      GO TO (901,902,903),I
  901 WRITE (66,104) RHO ,Z
  104 FORMAT(12X,8HCOPLANAR,21X,F6.4,16X,F6,4)
      GO TO 904
  902 WRITE(66,105)RHO,Z
  105 FORMAT (6X,20HPLANAR-PERPANDICULAR,15X,F6.4,16X,F6.4)
      GO TO 904
  903 WRITE(66,106) RHO,Z
  106 FORMAT(9X,15HCOPERPANDICULAR,17X,F6.4,16X,F6.4)
  904 K = K + 1
      GO TO (801,802,803),K
  803 XRM = XIR - XIM
      WRITE(66,225) XDQ,XQR,XAR,XDM,XAM,XIR,XRS,XRM
  225 FORMAT (/////"SUPPLEMENT"///"XDQ=",F10.4/
     1                             "XQR=",F10.4/
     1                             "XAR=",F10.4/
     1                             "XDM=",F10.4/
     1                             "XAM=",F10.4/
     1                             "XIR=",F10.4/
     1                             "XRS=",F10.4/
     1                             "XRM=",F10.4)
  808 CONTINUE
      READ(50,200) SENTNL
  200 FORMAT (I2)
      IF(SENTNL.EQ.0) STOP
      GO TO 1000
      END
```

```
      SUBROUTINE TRIG(S1,S2,RHYP,ANG)
C   THE SUBROUTINE CALCULATES TWO SIDES OF A RIGHT TRIANGLE IF ONE ANGLE AND
C         THE HYPOTENUSE ARE KNOWN
      S1 = RHYP*SIN(ANG)
      S2 = RHYP * COS(ANG)
      RETURN
      END
        .LOAD,,NOTYPE
```

APPENDIX B

Listing of Intermediate Case Geometry Program

```
$       TITLE   COMI  RESEARCH  INTERMEDIATE CASES
      REAL L
      DIMENSION NAME(80)
      RADIAN(ANGLE) = ANGLE * 0.01745
      DEGREE(ANGLE) = ANGLE / 0.01745
      TAN(ANGLE) = SIN(ANGLE)/COS(ANGLE)
      PI = 3.14159
 1000 READ(50,6) NAME
C  "NAME" CAN CONTAIN ALL DESCRIPTIVE INFORMATION THAT WILL FIT ON ONE CARD
    6 FORMAT(80A1)
C  THESE VALUES ARE OBTAINED FROM THE SUPPLEMENT OF THE "LIMITING CASE" PROGRAM
C         OUTPUT
      READ(50,1) XDQ,XQR,XAR,XDM,XAM,XIR,XRS,XRM
    1 FORMAT (8F7.4)
      WRITE (66,2) NAME
C  LABELS FOR FIRST SET OF VALUES
    2 FORMAT("1",80A1///"STATIONARY RING IN PLANE"////
     1       5X,"ANGLE OF ROTATION" ,5X, "RHO", 20X, "Z")
      THETA = -5.
C  THETA IS THE ANGLE OF ROTATION
C  THETA VARIED FROM 0 TO 180 DEGREES
      DO 100 I = 1,37
      THETA = THETA + 5.
      THETA = RADIAN(THETA)
      Z = XDQ * SIN(THETA)
      L = XDQ * COS(THETA)
      XNP = L * SIN(ATAN((XDM -XQR)/(XAM + XAR)))
      X = XQR + XNP
      XQP = L * COS(ATAN((XDM -XQR)/(XAM + XAR)))
      Y = XIR -XQP
      RHO = SQRT (X**2 + Y**2)
C  CHANGE RHO AND Z TO UNITS OF RING RADII
      RHO = RHO/1.3900
      Z = Z/1.3900
      THETA = DEGREE(THETA)
      WRITE(66,3) THETA, RHO,Z
    3 FORMAT(10X,F6.2,10X,F8.4,12X,F8.4)
  100 CONTINUE
      WRITE(66,4) NAME
C  LABELS FOR SECOND SET OF VALUES
    4 FORMAT ("1", 80A1///"STATIONARY RING OUT OF PLANE"////
     1       5X, "ANGLE OF ROTATION", 5X, "RHO", 20X, "Z")
      THETA = -5.
C  THETA VARIED FROM 0 TO 180 DEGREES
      DO 101 I = 1,37
      THETA = THETA + 5.
C  PHI IS THE COMPLEMENT IF THETA (THE ANGLE OF ROTATION)
      PHI = RADIAN(90.- THETA)
      X = SQRT((XRS**2 * XRM**2)/(XRM**2 + XRS**2 * (TAN(PHI)**2)))
      Y = (TAN(PHI)) * X
C  S1 AND S2 ARE SIDES OF THE TRIANGLE THAT HAS RHO FOR ITS HYPOTENUSE
 1001 S1 = XIR - Y
      S2 = X
      RHO = SQRT(S1**2 + S2**2)
      Z = ((XDM - XQR)/XRM) * Y + XQR
```

```
C  CHANGE RHO AND Z TO UNITS OF RING RADII
      RHO = RHO/1.3900
      Z = Z/1.3900
      WRITE(66,3) THETA, RHO, Z
  101 CONTINUE
      READ(50,5) SNTNL
    5 FORMAT (I2)
C  SENTINEL IS EITHER ZERO OR ONE
      IF(SNTNL.EQ.0) STOP
      GO TO 1000
      END
         .LOAD,NOTYPE
```

APPENDIX C

Listing of Table-Read Program

```
$        TITLE   PAT COMI   RESEARCH TABLE READ
      INTEGER END,STOP, GO, CONT,STAY
      DIMENSION NAME(80)
      COMMON RHO(42),Z(42), TABLE(42,2),IIII, JJJJ, DATA1, DATA2, II
      COMMON CONT
      A = 0.00
      DO 100 I = 1,42
      Z(I) = A
      RHO(I) = A
  100 A = A + 0.10
C RHO AND Z COORDINATES SET
      READ(50,2) MODE1,MODE2,END, STOP, GO,STAY
C  MODE1 MEANS COORDINATE INPUT, SHIFT OUTPUT
C  MODE 2 MEANS SHIFT INPUT, COORDINATE OUTPUT
C  THE PROGRAM CAN ONLY BE RUN UNDER ONE MODE AT A TIME
    2 FORMAT (3A3,3A4)
      READ(50,7) MODE
C  THIS DATA CARD DETERMINES UNDER WHICH MODE THE PROGRAM IS TO BE RUN
C  C>S  RUNS UNDER MOCE1
C  S>C   RUSN UNDER MODE2
    7 FORMAT(A3)
C MODE, END, AND CONTINUITY SPECIFICATIONS SET
 1004 READ(50,1) (TABLE(I,1),I = 1,42)
 1003 READ(50,1)( TABLE(I,2),I = 1,42)
C  THE DATA FOR MODE1 MUST FIRST BE ARRANGED BY THE INPUT Z COORDINATE.
C  THEY ARE GROUPED IN BLOCKS OF 0.00 - 0.09, 0.10 - 0.19, 0.20 - 0.29, ETC,
C  THE TABLE IS READ IN IN SEGEMNTS,   EACH SEGMENT CORRESPONDS TO THE RANGE OF
C  Z COORDINATES TO FOLLOW IT.
    1 FORMAT (10F8.5)
C TABLE SET
      WRITE(66,10)
   10 FORMAT(1H1)
C  IIII AND JJJJ ARE INDEXING PARAMETERS USED IN LABLEING
      IIII = 0
      JJJJ = 0
 1005 READ (50,8) NAME
C  "NAME" CONTAINS ALL DESCRIPTIVE INFORMATION THAT WILL FIT ON ONE CARD.
    8 FORMAT (80A1)
      WRITE (66,8) NAME
 1000 READ(50,3) DATA1, DATA2
C  DATA1 AND DATA2 ARE RHO AND Z IF RUN UNDER MODE1.
C  DATA1 IS THE COORDINATE VALUE AND DATA2 IS NOT USED IF RUN UNDER MODE2
    3 FORMAT(2F20.5)
C DATA CARD IN
C  II IS AN INDEXING PARAMETER USED IN INTERPOLATION.  IT CORRESPONDS TO A
C  RANGE OF RHO VALUES
      II = DATA2 * 10. + 1.
 1001 IF(MODE.EQ.MODE1) CALL SHIFT
      IF(MODE.EQ.MODE2) CALL COORD (STOP)
C MODE DETERMINED AND SUBROUTINES CALLED
      READ(50,6) CONT
C  CONT IS THE CONTINUITY CARD
C  THERE ARE 4 POSSIBLE CONTINUITY STATES
C     STAY MENAS THAT THE SAME TABLE SEGMENT WILL BE USED FOR THE NEXT DATA
C           CARD
C     GO MEANS THAT A COMPLETELY NEW SEGMENT OF THE TABLE WILL BE READ IN
```

```
C             FOR A NEW RANGE OF DATA
C       END MEANS THAT ONLY HALF OF A TABLE SEGMENT WILL BE READ IN BECAUSE THE
C             UPPER BOUND OF THE PROVIOUS RANGE IS TO BECOME THE LOWER BOUND OF T
C             THE NEW RANGE
C       STOP WILL HALT THE RUN
    6 FORMAT (A4)
      IF(CONT.EQ.STAY) GO TO 1005
      IQ = II + 1
C  LABELS AND TABLE SEGMENT USED WRITTEN
 1002 WRITE(66,4) (Z(J),J = II,IQ)
    4 FORMAT (1H1,2(10X, F10.2)///)
      DO 101 I = 1,41
      WRITE(66,5) RHO(I), (TABLE(I,J), J = 1,2)
    5 FORMAT(F6.3,2F20.5)
  101 CONTINUE
      IF(CONT.EQ.STOP) STOP
      IF (CONT.EQ.GO) GO TO 1004
      DO 102 I = 1, 42
  102 TABLE(I,1) = TABLE(I,2)
      GO TO 1003
      END
```

```
      SUBROUTINE SHIFT
      COMMON RHO(42),Z(42), TABLE(42,2),IIII, JJJJ, DATA1, DATA2, II
      COMMON CONT
      IIII = IIII + 1
      IF(IIII.GT.1) GO TO 1006
      WRITE(66,1)
C  LABELS FOR COLUMN HEADINGS
    1 FORMAT (" COORDINATES TO SHIFT"//// 10X,"RHO",10X,"Z",10X,"SHIFT"
     1 ///)
 1006 DO  100 I = 1,41
C  SCAN TABLE FOR RANGE OF RHO
      IF(DATA1.GE.RHO(I).AND.DATA1.LT.RHO(I + 1))GOTO 1000
  100 CONTINUE
C  INTERPOLATION FOR RHO RANGE IN LOWER BOUND OF Z VALUE
 1000 CALL INTER (RHO(I +1), RHO(I), DATA1, TABLE(I + 1, 1),
     1 TABLE(I,1), A)
C  INTERPOLATION FOR RHO RANGE IN UPPER BOUND OF Z VALUE
      CALL INTER (RHO(I + 1), RHO (I), DATA1, TABLE(I + 1,2),
     1 TABLE(I,2), B)
C  INTERPOLATION TO DESIRED SHIFT VALUE
      CALL INTER (Z(II + 1), Z(II), DATA2, B, A, C)
C  OUTPUT:  COORDINATES AND SHIFT
      WRITE(66,2) DATA1,DATA2,C
    2 FORMAT(3F12.5)
      RETURN
      END
```

```
      SUBROUTINE COORD (STOP)
      COMMON RHO(42),Z(42), TABLE(42,2),IIII, JJJJ, DATA1, DATA2, II
      COMMON CONT
      WRITE(66,1)
C  LABELS FOR COLUMN HEADINGS
    1 FORMAT("1SHIFT TO COORDINATES" //// 10X, "SHIFT", 10X, "RHO",10X,
     1  "Z"///)
      JJJJ = JJJJ + 1
      IF (JJJJ.GT.1) GO TO 1003
C  A AND K ARE CHECKING PARAMETERS ON TABLE SCANNING
 1003 A = 0.000
      K = 0
 1002 A = A + 0.001
      DO 100 I = 1,41
C  SCAN TABLE FOR COORDINATE VALUE NEAR THAT OF INPUT VALUE
      IF (ABS(DATA1 - TABLE(I,1)).LT.A) GO TO 1000
      GO TO 1001
C  INTERPOLATE TO FIND Z COORDINATE
 1000 CALL INTER (TABLE(I,2), TABLE(I,1), DATA1, Z(II + 1), Z(II), B)
C  INTERPOLATE TO FIND RHO COORDINATE   OUTPUT:  SHIFT AND COORDINATES
      CALL INTER(TABLE(I + 1,2), TABLE(I,1), DATA1, RHO(I + 1),
     1 RHO(I), C)
C  OUTPUT:  SHIFT AND COORDINATES
      WRITE(66,2) DATA1,C,B
    2 FORMAT (3F12.5)
      K = K + 1
C  CHECK TO SEE THAT ALL POSSIBLE COORDINATE VALUES ARE TRIED
 1001 IF(I.EQ.41.AND.K.EQ.0.AND.A.LT.0.005) GO TO 1002
  100 CONTINUE
      READ(50,3) CONT
C  SAME CONTINUITY REQUIREMENTS AS FOR MAIN PROGRAM
    3 FORMAT(A4)
      IF(CONT.EQ.STOP) STOP
      DO 111 I = 1, 42
  111 TABLE(I,1) = TABLE(I,2)
      READ(50,4)( TABLE(I,2),I = 1,42)
    4 FORMAT (10F8.5)
C  THIS SUBROUTINE DOES NOT RETURN TO THE MAIN PROGRAM
      GO TO 1003
      RETURN
      END
```

```
      SUBROUTINE INTER (A,B,C,D,E,ANS)
      ANS = E + (D - E) * ((C - B)/(A - B))
      RETURN
      END
```