I. ELECTRON SPIN RESONANCE OF CYCLOHEPTATRIENYL

II. AUXILIARY APPARATUS

Thesis by

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ABSTRACT

Part I. The ESR spectra of cycloheptatrienyl (CHT) in several crystalline environments at temperatures ranging from 1.5° to 300°K and the methods of sample preparation are described in detail.

The observed spectra are classified as:

(a) High-temperature spectra — eight equally spaced lines with splittings of 3.7 to 4 gauss and intensity ratios 1:7:21:35:35:21:7:1.

(b) Low-temperature spectra — highly anisotropic and different for each environment.

The transitions between (a) and (b) are abrupt, and the transition temperatures are different for each environment.

CHT is a planar regular heptagon with an orbitally degenerate ground state. This degeneracy can be removed by a crystalline electric field. The wave functions, after the degeneracy has been removed, are determined by the crystal field. The Jahn-Teller distortion of the ring and the spin-orbit interaction are probably less than 1 cm^{-1}.

Part II. The low-temperature ESR system used in the study of CHT is described in detail. A simple and effective zone refiner for organic compounds is described.

ABSTRACT OF PROPOSITIONS

1. An extremely versatile low-temperature ESR system is described in detail.
2. The vapor phase photolysis of cyclopropene to produce cyclopropenyl radical (C_3H_3) for study by ESR is proposed.
3. An experiment to measure the pi-electron spin-orbit interaction in CHT is proposed.
4. It is proposed that magnetic rotation spectroscopy be used to search for the second and third triplet states of benzene.
5. Bitropyl-thiourea inclusion compound is proposed as a novel triplet exciton system.

TABLE OF CONTENTS

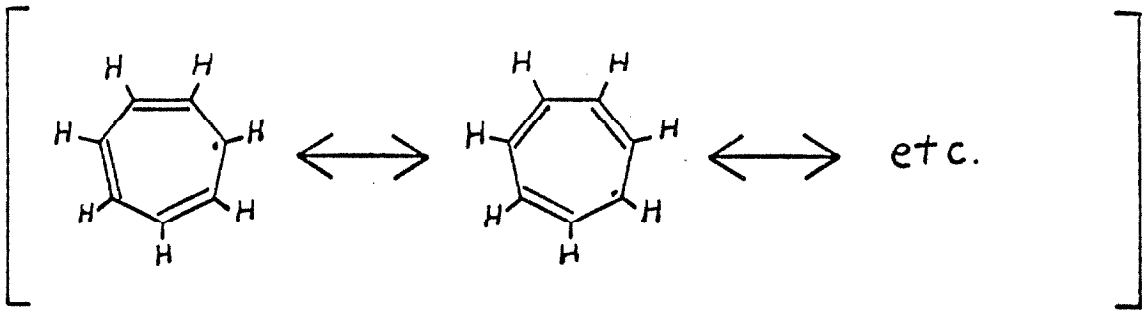
(TABLE OF CONTENTS. Continued)

PART I

ELECTRON SPIN RESONANCE OF CYCLOHEPTATRIENYL

A. INTRODUCTION

At the time this study was begun, very little was known about the cycloheptatrienyl radical (CHT). Its



existence had been inferred by mass spectrometry (1).

CHT is a particularly interesting free radical for study by electron spin resonance (ESR). It is a non-alternant pi-orbital radical. The LCAO-MO and the valence bond methods predict an orbitally degenerate ground state (2,3). However, the Jahn-Teller theorem (4) predicts that if the ground state were degenerate, then distortion of the ring would remove the degeneracy.

Thus, the following questions arise: a) Is CHT a planar regular heptagon? b) Is the ground state orbitally degenerate? c) What is the pi-electron wave function? A detailed study of the oriented CHT radical by ESR should give the answers.

Part I of this thesis describes the successful ESR study of both oriented and polycrystalline CHT radicals at temperatures from 300° to 1.5°K. Part II describes the special apparatus constructed to make these experiments possible.

After the author's preliminary results were published (5), two other laboratories reported the ESR of CHT. Dos Santos-Veiga (6) studied CHT in solution; Arai et al. (7) studied CHT in polycrystalline form, but neither reported the dependence of the ESR spectrum on temperature.

B. CYCLOHEPTATRIENYL-NAPHTHALENE

Preparation of Samples

By irradiating a dilute solid solution of cycloheptatriene* in naphthalene with 50 kilovolt tungsten x-rays, the author obtained the CHT radical in moderate concentration (Fig. 1a). The naphthalene should be purified by zone refining** in order to obtain good quality single crystals and to keep x-ray-damaged impurities from interfering with the ESR of CHT.

The crystal growing method is essentially that of Bridgman (8). Naphthalene and approximately 5% cycloheptatriene are sealed together into a pyrex crystal-growing tube under a low pressure (~5 mm Hg) nitrogen or helium atmosphere in order to retard sublimation. The contents of the tube are melted and then frozen from one end at the rate of 2.5 cm/day. The freezing is started by touching the end of the tube with a wetted fingertip in order to avoid supercooling. A schematic diagram of the crystal-growing apparatus is shown in Figure 2. The constriction near the bottom of the tube is for the purpose of selecting one crystal from the many seeds at the beginning of the solidification.

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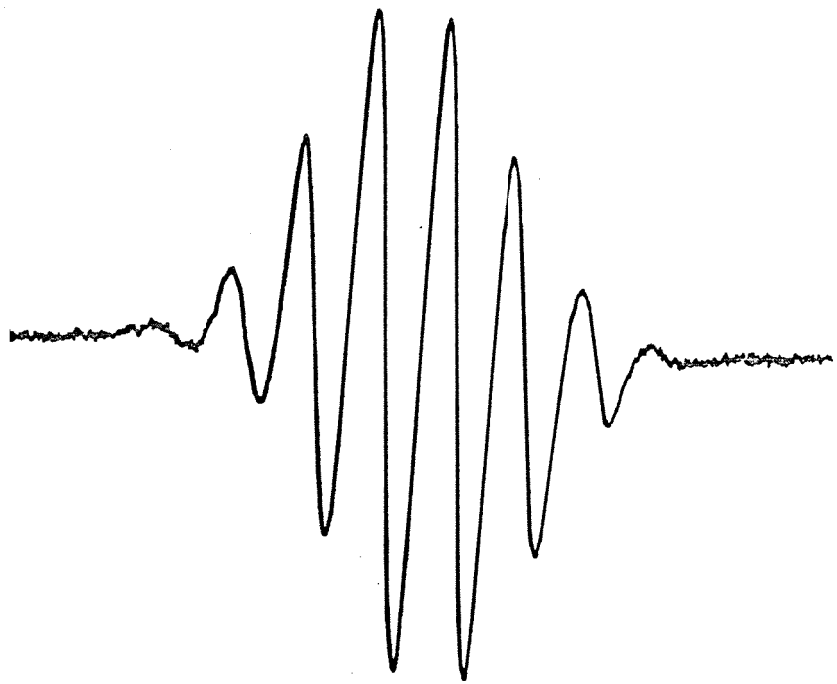
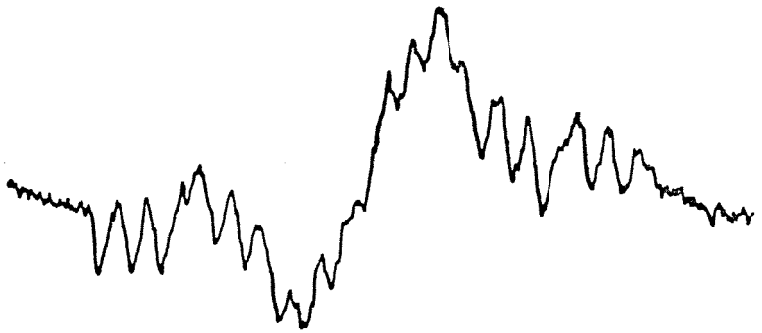
*Cycloheptatriene from K & K Laboratories, Inc., and from Columbia Organic Chemicals Co., Inc., both gave identical results.

**See Part IIB of this thesis.



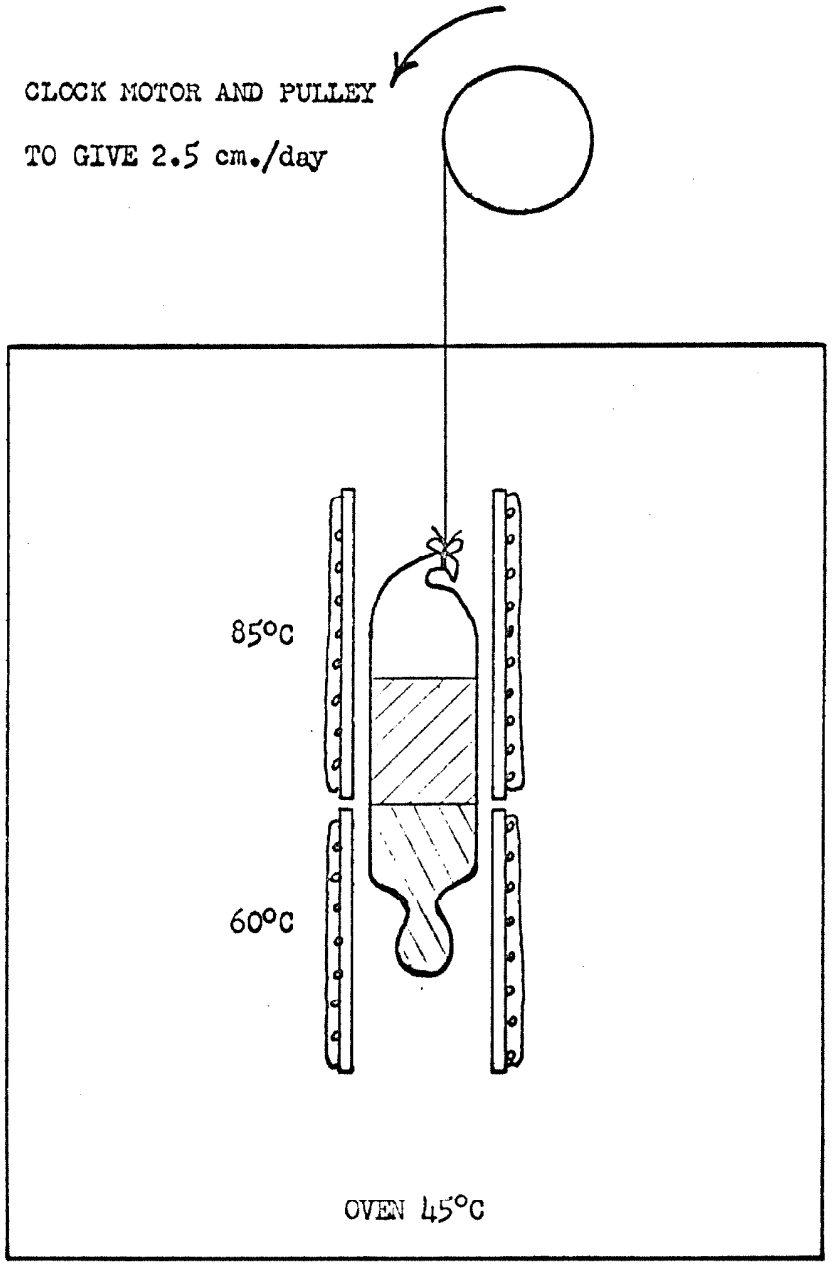
(a)

FIGURE 1. (a) CHT in naphthalene at room temperature. $H_o \parallel$ a axis.



(b)

FIGURE 1. (b) Cycloheptatriene in naphthalene (powder) x-irradiated in absence of O_2 (not to same scale).



HEATERS ARE RESISTANCE WIRE WOUND ON ALUMINUM TUBES AND COVERED WITH ASBESTOS.

FIGURE 2. Crystal grower for naphthalene-cycloheptatriene mixed crystals.

After crystal growth, the tubes are broken open and the crystals are removed. They are clear and easily cleaved. The cleavage plane is usually either inclined 60° to the tube axis or parallel to it.

If the sample is thoroughly degassed, sealed, and x-irradiated under an almost oxygen-free atmosphere (sodium-potassium alloy trap), large amounts of free radicals in addition to CHT are formed (Fig. 1b). Oxygen in very low concentration is apparently necessary to scavenge the hydrogen atoms formed by x-irradiation of cycloheptatriene.

Before irradiation the crystals may be kept under an inert atmosphere for a long period without deteriorating appreciably; however, leaving them a few days in the atmosphere apparently destroys the cycloheptatriene (ozone?) because only a broad unresolved resonance is observed after irradiation. Once formed, the CHT radicals are surprisingly stable. Samples have been kept in air at room temperature for one month with a reduction in CHT concentration of only one-half. Irradiation times of 10 to 20 hours at 50 kilovolts, 32 milliamps have been used.

The naphthalene crystal structure has been studied in detail by Robertson (9,10). See Fig. 3. Naphthalene is monoclinic prismatic, $a = 8.235$, $b = 6.003$, $c = 8.658$ Å, and $\beta = 122^{\circ}55'$. The space group is $C_{2h}^{5}(P2_1/a)$, with two molecules per unit cell. The molecular symmetry in the

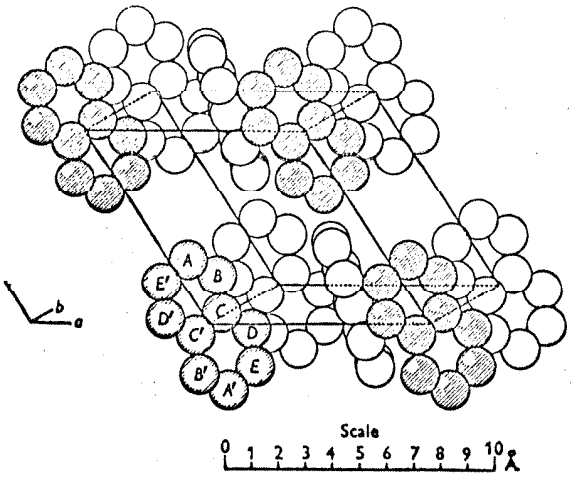


Figure 3. Naphthalene. Molecular arrangement in the unit cell. After Robertson (10).

crystal is $\bar{1}$. It is assumed that each CHT replaces substitutionally one naphthalene molecule. The normals (N) to the CHT plane (assuming for the moment that it is planar) would then make the following angles with the crystal axes: $N \wedge a = 32.8^{\circ}$, $N \wedge b = 116.3^{\circ}$, $N \wedge c = 71.9^{\circ}$. The molecules will be magnetically equivalent when H_o lies in the ac plane or is parallel to the b axis.

The orientation of the crystals was determined by the optical axes, the cleavage plane, and the extinction directions under a polarizing microscope (11). Flat surfaces, in addition to the cleavage plane, for mounting the crystal can easily be cut with a razor blade. For low temperature experiments, the crystals were attached to the crystal mount* with an adhesive (Kwiram Glue) made

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*See Part IIA of this thesis.

from General Electric Insulating Varnish and Adhesive #7031 by mixing it in a 1:1 ratio with toluene (12). The adhesive was spread in a very thin layer onto the crystal mount and immediately the crystal was pressed against it. It was allowed to set for approximately 45 minutes before use. The naphthalene crystals do not shatter when cooled slowly to 4.2°K, and the adhesive holds them firmly at all temperatures.

Experimental Results

The CHT-naphthalene ESR spectrum between 20° and 300°K (high-temperature spectrum) consists of eight equally spaced lines with intensity ratios 1:7:21:35:35:21:7:1 (Fig. 1a). The spectrum is slightly anisotropic, as can be seen in Table I. As compared to other free radicals in the solid state, microwave saturation is difficult to attain, and it does not cause much change in the shape of the spectrum. The C^{13} splittings for carbon in natural abundance were not observed.

Cooling the CHT-naphthalene from 300° to 30°K broadens the spectrum slightly. Cooling from 30° to 20°K broadens the spectrum much more. When cooled through a one or two-degree interval near 20°K the hyperfine structure (hfs) changes radically* (Fig. 4). There is no further change as the crystal is cooled to 4.2°K. This low-temperature spectrum is highly anisotropic. The

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*The g value, however, does not change appreciably when H_o is parallel to the a axis.

apparent number of lines varies from three to seven when the magnetic field H_o is in the ac plane (Figs. 5-9). The effect of microwave saturation on the low temperature spectrum is shown in Fig. 10. The individual lines are not resolved in the low temperature spectrum, but the minima of slope, maxima of slope, and zeros of the absorption curve are listed in Table II for the magnetic field H_o lying in the ac plane of the crystal.

TABLE I. Cycloheptatrienyl in Naphthalene, High-Temperature Form

Temp.	Orientation	hfs*	hfsx7	Line Width**	g Value***
300°K	$H_o \parallel a$	4.08	28.5	1.83	2.0035
300	$H_o \parallel b$	3.75	26.3	1.64	2.0037
300	$H_o \parallel c$	3.56	24.9	1.47	2.0038
300	powder	3.75	26.3	2.00	2.0035

*Hyperfine splitting (gauss).

**Full width between maximum slope and minimum slope (gauss).

***Polycrystalline diphenyl picryl hydrazyl (13) was used as an internal standard. The absolute values should be correct to ±.0004 while the relative values should be correct to ±.0001.

TABLE II. Cycloheptatrienyl in Naphthalene, Low-Temperature Form

θ*	First (low-field) point of max. slope to the successive points of max. slope (1st row) and to the points of min. slope (2nd row) of the ESR absorption curve (gauss)											First point (0.0) to point of zero slope (gauss)					
0°	0.0	5.8	11.6	22.0	29.1	. .	. .	. .	. .	. .	. .	. .	. .	. .	15.8	. .	. .	. .
	2.6	10.0	20.2	25.7	31.7	. .	. .	. .	. .	. .	. .							
18	0.0	6.3	13.1	21.1	29.2	. .	. .	. .	. .	. .	. .	. .	. .	. .	15.4	. .	. .	. .
	3.1	11.1	19.1	26.6	32.1	. .	. .	. .	. .	. .	. .							
30	0.0	7.2	12.1	19.7	27.8	. .	. .	. .	. .	. .	. .	. .	. .	. .	15.2	. .	. .	. .
	3.5	11.5	19.0	24.5	31.7	. .	. .	. .	. .	. .	. .							
40	0.0	6.7	9.0	17.0	22.9	28.2	. .	. .	. .	. .	. .	. .	. .	14.0	15.9	17.3	. .	. .
	3.3	8.6	14.4	22.2	24.6	31.4	. .	. .	. .	. .	. .							
50	0.0	6.0	10.2	17.5	22.6	28.5	. .	. .	. .	. .	. .	. .	. .	13.1	15.8	18.7	. .	. .
	3.2	8.8	14.1	21.4	25.5	31.5	. .	. .	. .	. .	. .							
60	0.0	5.1	9.9	15.0	18.2	23.5	28.3	. .	. .	. .	. .	. .	12.4	13.8	15.6	17.1	19.0	. .
	2.8	7.4	12.9	15.9	21.4	25.9	31.1	. .	. .	. .	. .							
70	0.0	5.3	10.0	14.7	19.2	24.3	29.4	. .	. .	. .	. .	. .	12.1	13.3	16.0	18.7	19.5	. .
	2.9	7.9	12.7	17.1	22.1	26.8	32.0	. .	. .	. .	. .							
80	0.0	5.5	10.3	15.1	20.0	24.5	29.4	. .	. .	. .	. .	. .	12.7	13.4	16.4	19.5	20.2	. .
	3.1	8.2	13.2	17.6	22.6	27.3	32.8	. .	. .	. .	. .							
90	0.0	2.3	8.1	13.3	18.1	23.3	26.8	32.6	38.0	. .	. .	. .	. .	. .	19.3	. .	. .	. .
	0.7	5.8	11.6	15.6	20.5	25.5	30.0	36.1	38.9	. .	. .							
100	0.0	6.3	15.0	22.2	30.2	. .	. .	. .	. .	. .	. .	. .	. .	. .	17.3	. .	. .	. .
	4.2	12.6	19.8	28.1	34.5	. .	. .	. .	. .	. .	. .							
108	0.0	6.4	14.0	22.3	31.3	. .	. .	. .	. .	. .	. .	. .	10.2	11.4	16.4	21.7	22.7	. .
	2.3	10.7	18.9	26.4	33.5	. .	. .	. .	. .	. .	. .							
120	0.0	6.8	15.6	22.6	32.4	. .	. .	. .	. .	. .	. .	. .	10.5	12.9	17.1	22.2	23.7	. .
	2.7	11.8	19.2	27.7	34.4	. .	. .	. .	. .	. .	. .							
130	0.0	6.4	15.0	22.0	31.2	. .	. .	. .	. .	. .	. .	. .	10.5	11.9	16.4	21.4	22.4	. .
	2.0	11.1	18.2	26.4	33.0	. .	. .	. .	. .	. .	. .							
140	0.0	2.4	5.5	8.7	15.3	18.0	21.0	25.3	31.5	33.8	37.2	. .	12.4	14.0	19.1	24.1	28.2	. .
	0.6	4.4	6.8	13.2	17.3	20.6	22.8	29.7	32.3	35.6	37.6							
150	0.0	6.2	12.4	16.7	22.8	28.8	. .	. .	. .	. .	. .	8.9	10.5	14.7	16.0	17.3	22.1	23.5
	3.4	9.7	15.5	20.3	26.6	32.6	. .	. .	. .	. .	. .							
160	0.0	6.0	12.0	17.5	23.0	29.0	. .	. .	. .	. .	. .	8.5	10.3	13.7	16.5	18.3	22.3	23.7
	3.1	9.5	14.8	20.4	26.4	32.1	. .	. .	. .	. .	. .							
170	0.0	5.9	11.1	16.4	22.7	29.1	. .	. .	. .	. .	. .	. .	. .	. .	15.9	. .	. .	. .
	2.4	9.0	15.3	19.9	25.8	31.3	. .	. .	. .	. .	. .							
$H_o \parallel$ CHT normal	0.0	6.6	13.3	21.4	28.0	. .	. .	. .	. .	. .	. .	. .	. .	. .	15.4	. .	. .	. .
	4.3	10.9	18.3	24.9	31.3	. .	. .	. .	. .	. .	. .							

*θ is the angle between H_o and the a axis of the crystal measured toward c . H_o lies in the ac plane except for the last entry in the table where it makes an angle of 28° with the ac plane.

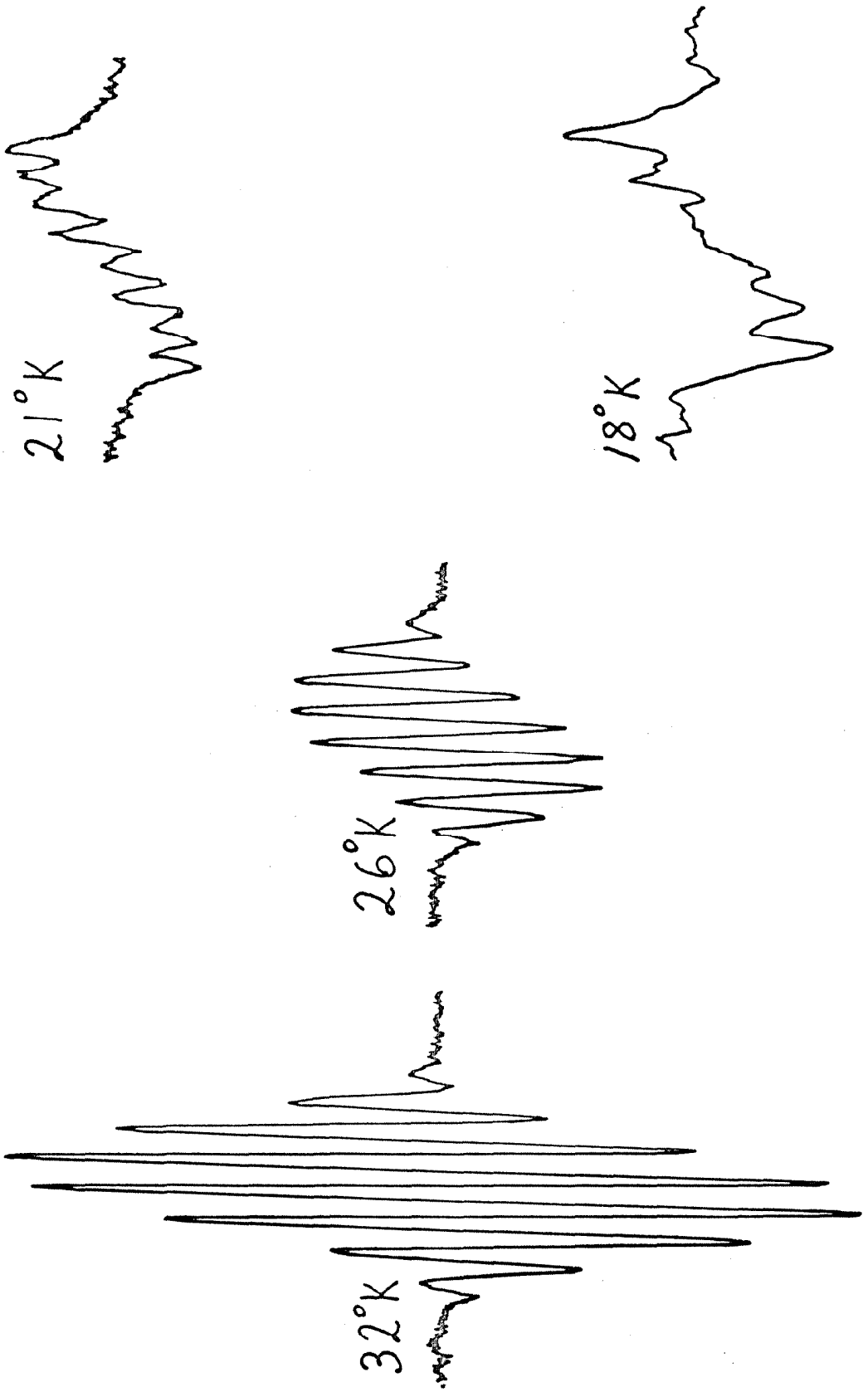


FIGURE 4. Transition of CHT in naphthalene. H_o // a axis.

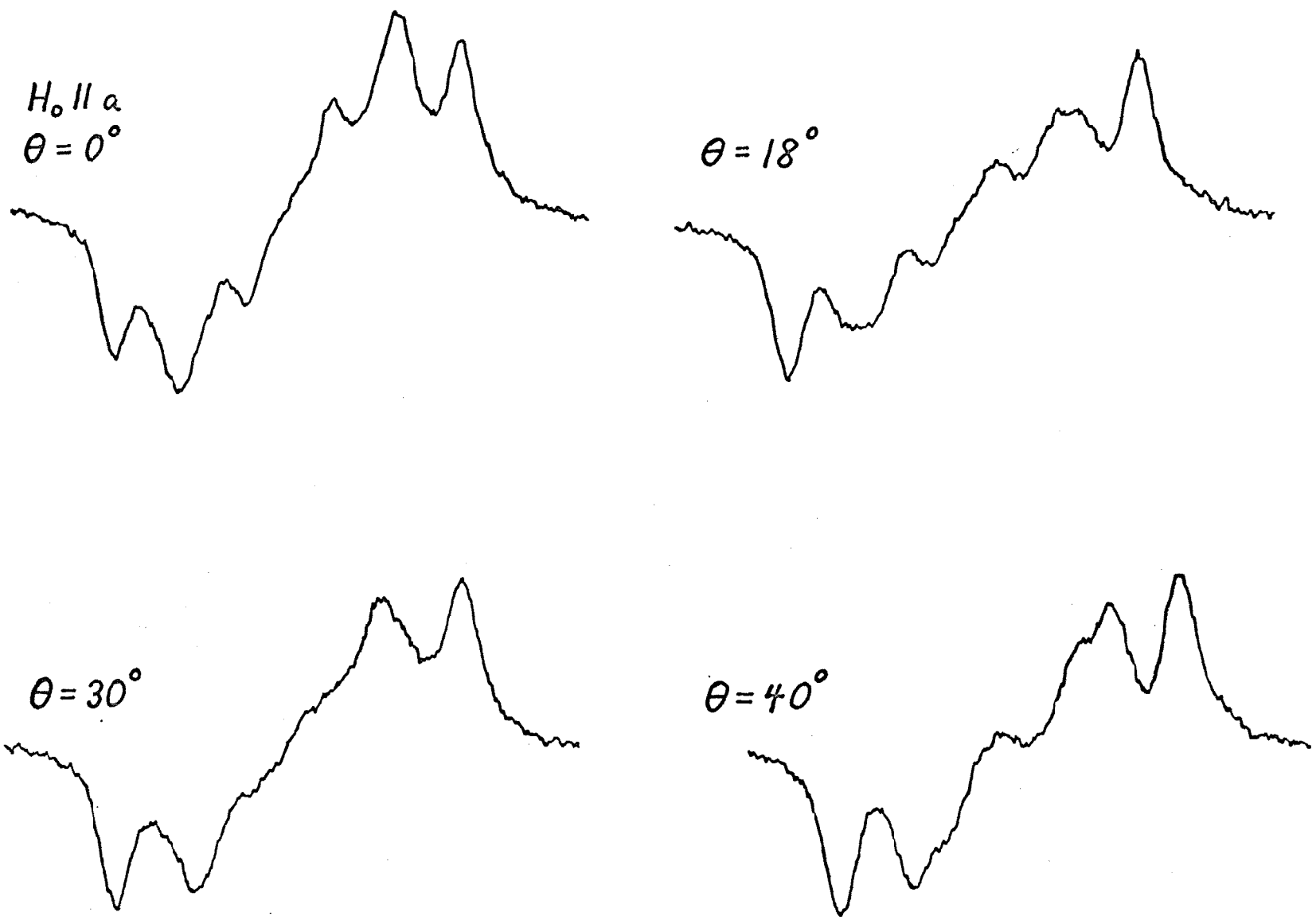


FIGURE 5. Low-temperature spectra of CHT in naphthalene.

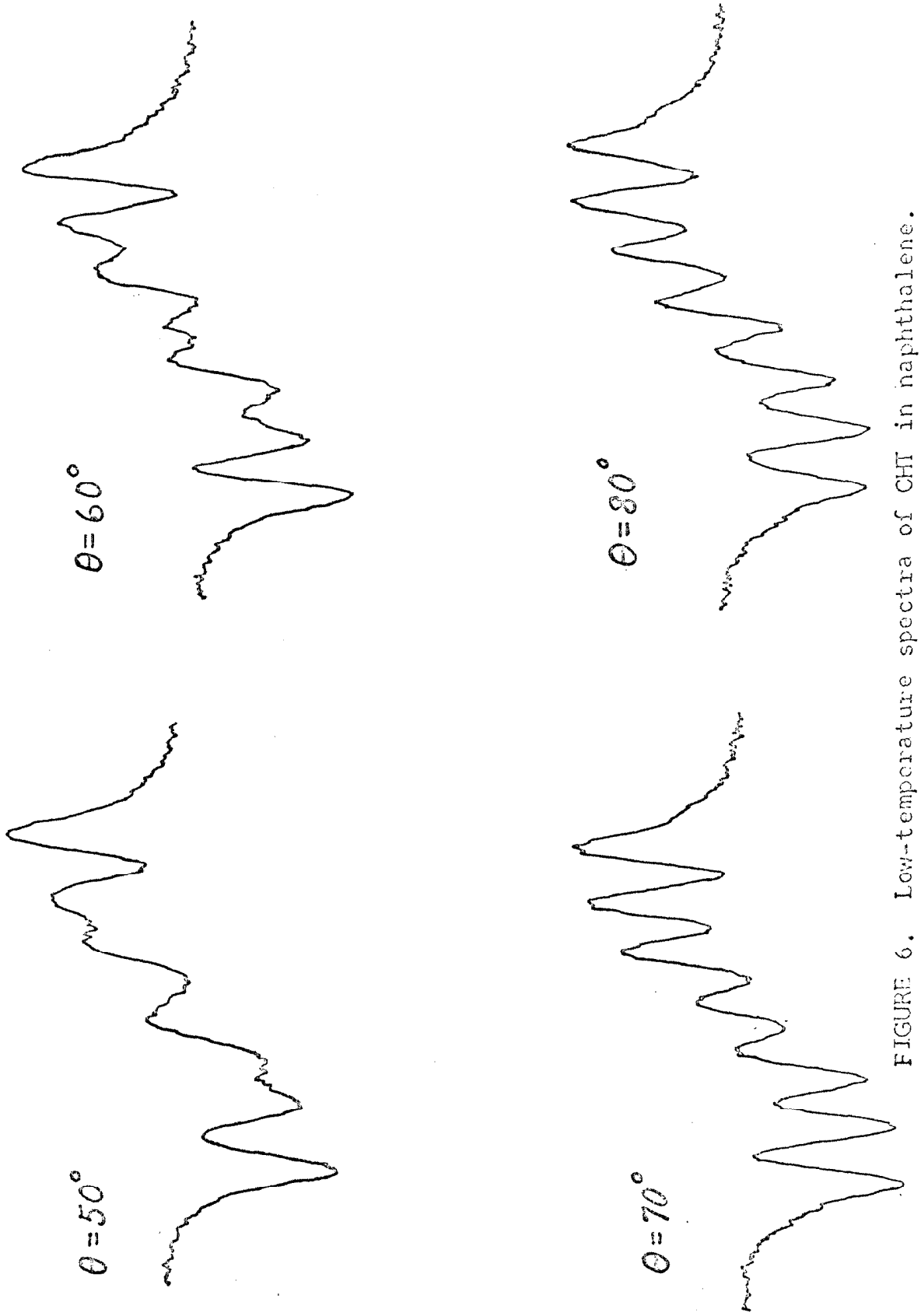


FIGURE 6. Low-temperature spectra of CHT in naphthalene.

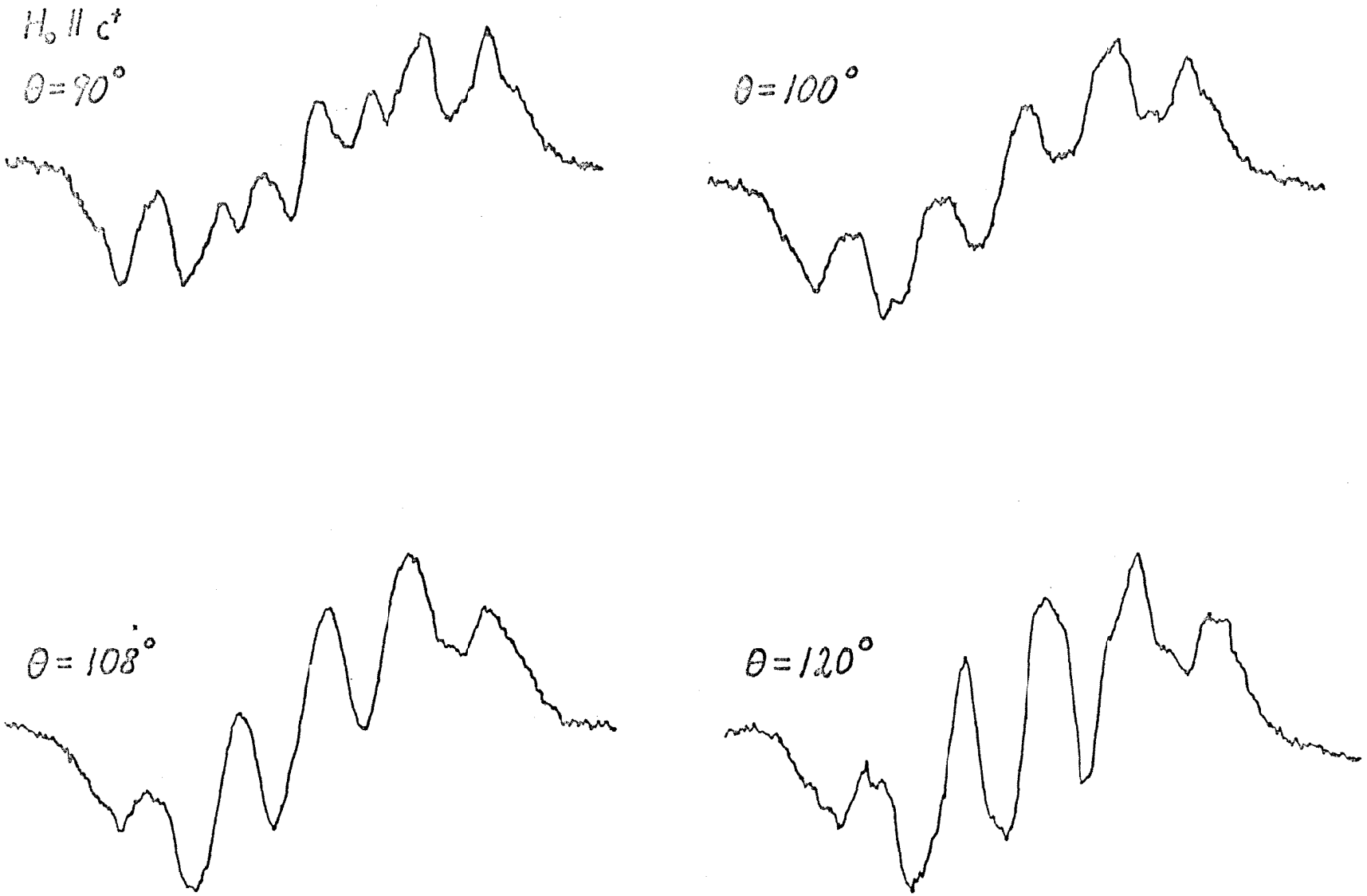


FIGURE 7. Low-temperature spectra of CHT in naphthalene.

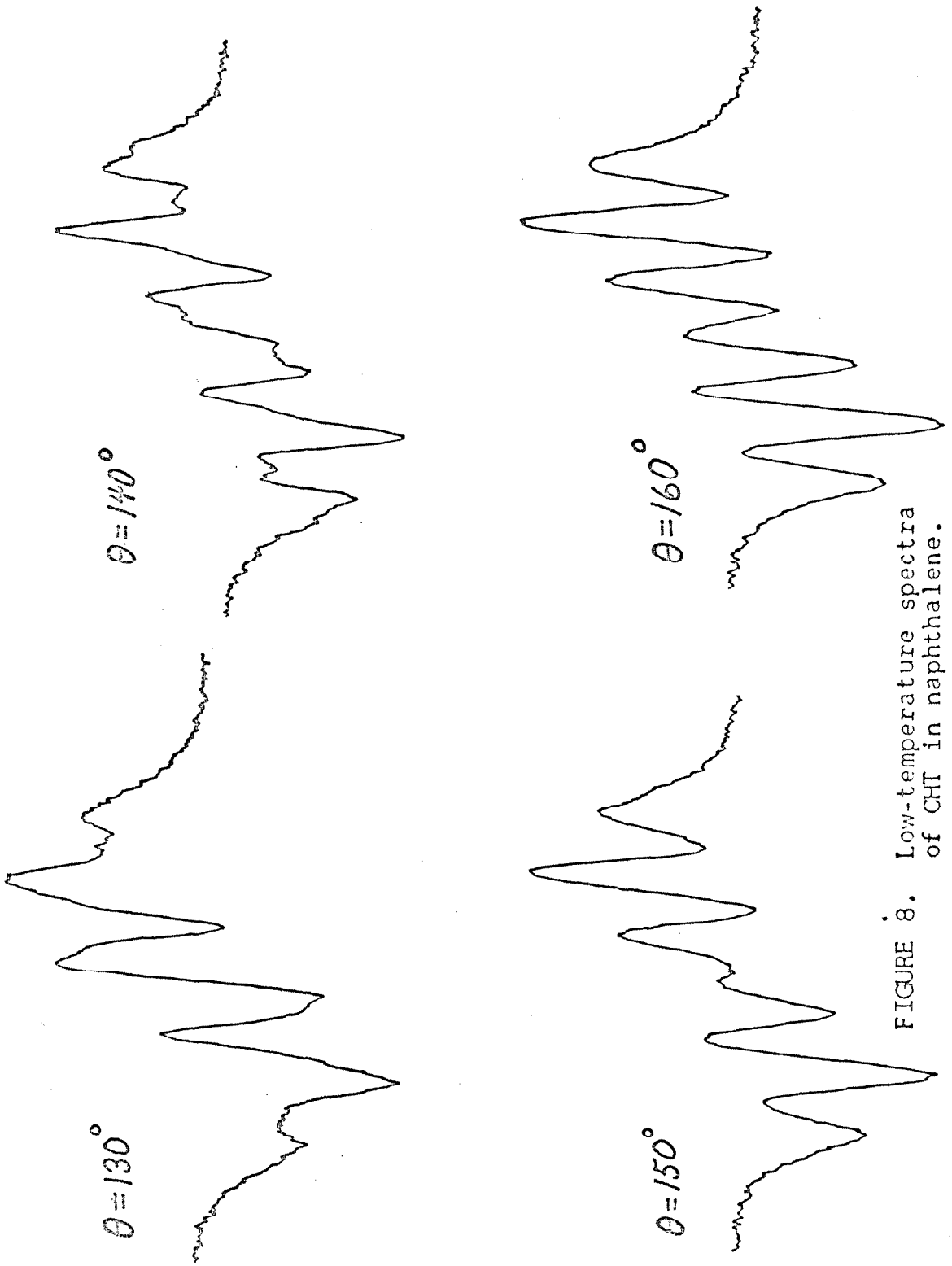


FIGURE 8. Low-temperature spectra of CHT in naphthalene.

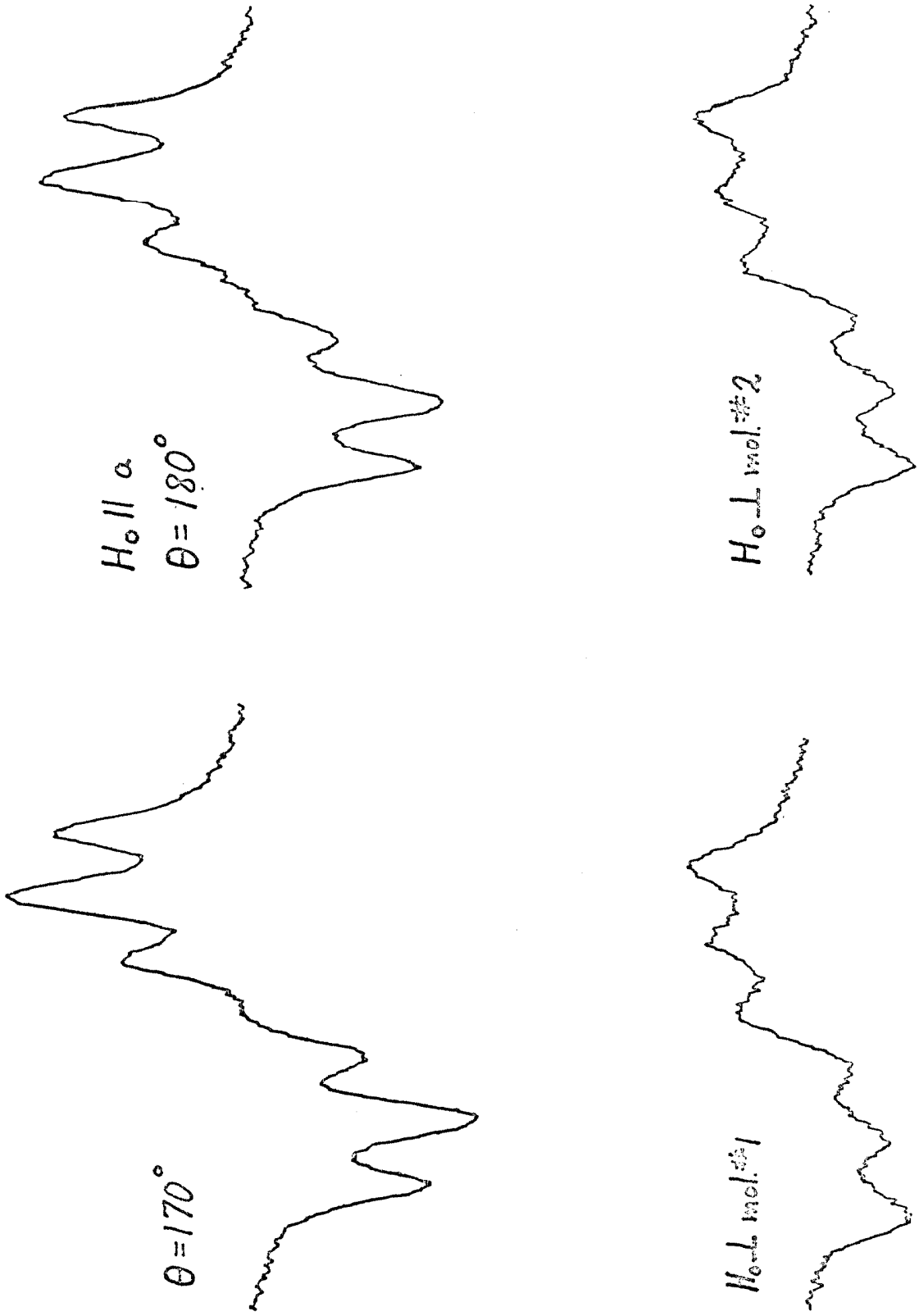
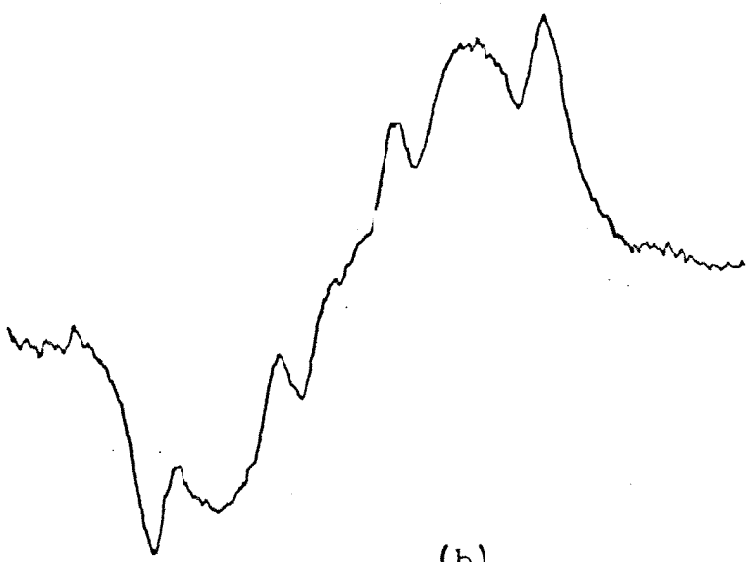
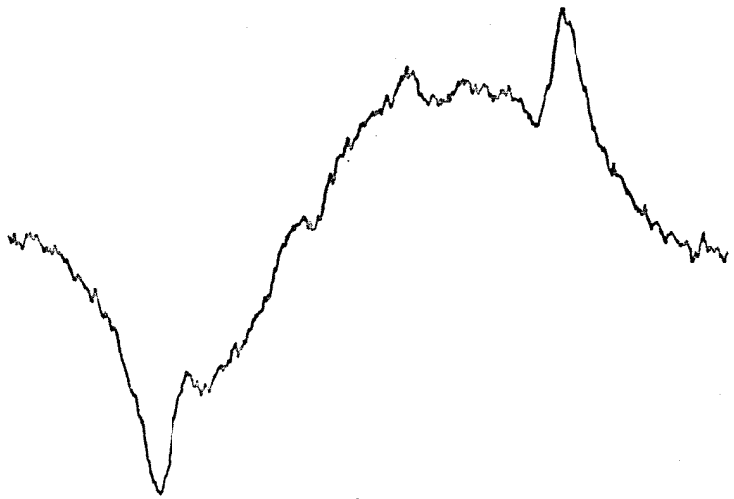


FIGURE 9. Low-temperature spectra of CHI in naphthalene.

(a)



(b)



(c)

FIGURE 10. Effect of microwave saturation on CHT in naphthalene. (a) (b) and (c) are in order of increasing power, $H_o \parallel$ a axis.

C. CYCLOHEPTATRIENYL-THIOUREA

Preparation of Samples

O. Hayes Griffith suggested to the author that a thiourea-cycloheptatriene inclusion compound (14) could prove useful in the ESR study of CHT. Indeed, a white powder immediately formed upon shaking an aqueous solution of thiourea with cycloheptatriene. After x-irradiation the powder gave the characteristic eight-line CHT spectrum with very little interference from other free radical species.

Many cyclic or highly branched organic molecules form inclusion compounds with thiourea (15). Von Lenné (16) has shown by x-ray crystallography that no chemical bonds are formed between the host lattice (made of thiourea) and the included molecules. The size of the included molecules and not their functional groups determines whether or not the inclusion compound can be formed. The thiourea base lattice belongs to the space group $R\bar{3}2/c$ with $a \approx 15.8$ Å and $c \approx 12.5$ Å. The included molecule fits into the hexagonal canal or tube formed by the thiourea molecules (Fig. 11). The hexagonal canal has a minimum width varying from 7.4 Å at the points designated 32 to 6.4 Å half-way between the 32 points.

In the case of the cyclohexane-thiourea inclusion compound, the cyclohexane, even though not restricted purely by geometrical size, enters into the host lattice only at the sites of 32 symmetry (16). All cyclohexane

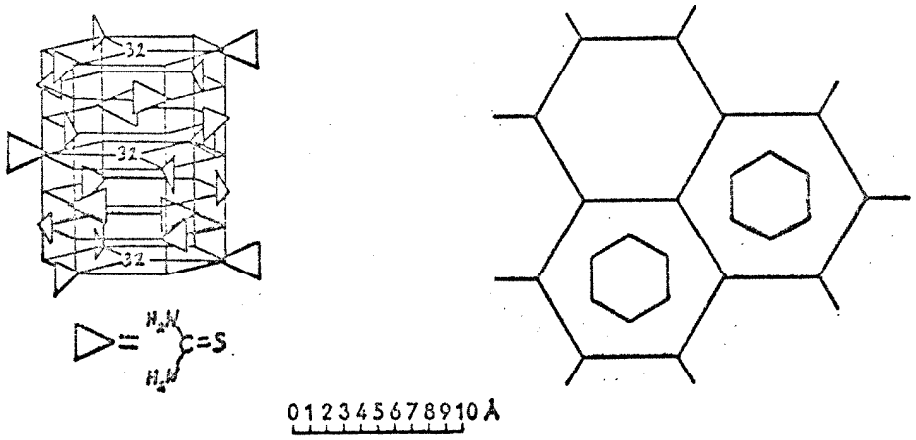


Figure 11. Thiourea inclusion compound base-lattice with cyclohexane drawn in. After von Lenne (16).

molecules are required to be parallel. However, the cyclohexane molecule can be twisted to any arbitrary angle about its 6-fold axis. Furthermore, it appears that the cyclohexane is oscillating rapidly about its 6-fold axis and is also rotating about arbitrary axes in the molecular plane. It is probable that CHT fits into the thiourea lattice in much the same manner as cyclohexane.

The problem of making a large single crystal took quite some time and effort to solve. It was eventually found that long, thin, hexagonal needles could be obtained by slowly cooling a solution of thiourea and cycloheptatriene in absolute methanol. If too much thiourea is used, thiourea crystals with much the same crystal habit as that of the inclusion compound will also be formed. Unfortunately, after x-irradiation, inclusion compound crystals formed in this manner exhibited an unwanted ESR

absorption with a g value very close to that of CHT and a partially resolved hyperfine structure twice as wide (Fig. 12). It was found that either a faster precipitation or a higher concentration of cycloheptatriene reduces the amount of this unwanted radical. When ethanol is used instead of methanol, a stronger, completely unresolved impurity resonance is observed. This makes it apparent that the alcohol is being included along with cycloheptatriene and consequently will also be damaged by the x-irradiation. It proved impossible to make the inclusion compound without a solvent because the thiourea would not dissolve in cycloheptatriene. However, the impurity resonance from methanol can be reduced to approximately 1% of the total CHT spectrum by using equal parts of cycloheptatriene and methanol, even though cooled very slowly. This impurity resonance becomes too broad to observe when cooled to 77°K, so that it interferes very little with the CHT spectrum.

The following procedure was finally devised for making large single crystals of cycloheptatriene-thiourea inclusion compound: seal under vacuum 1 ml cycloheptatriene, 1 ml absolute methanol, and 0.1 g thiourea in an 11 mm tube which has one end drawn to a point. Heat the tube until the thiourea has completely dissolved. Then place the tube, point down, in an oven at 50°C. Heat the upper half of the tube with a resistance coil to a few degrees above the temperature of the oven. Allow the oven to cool over a

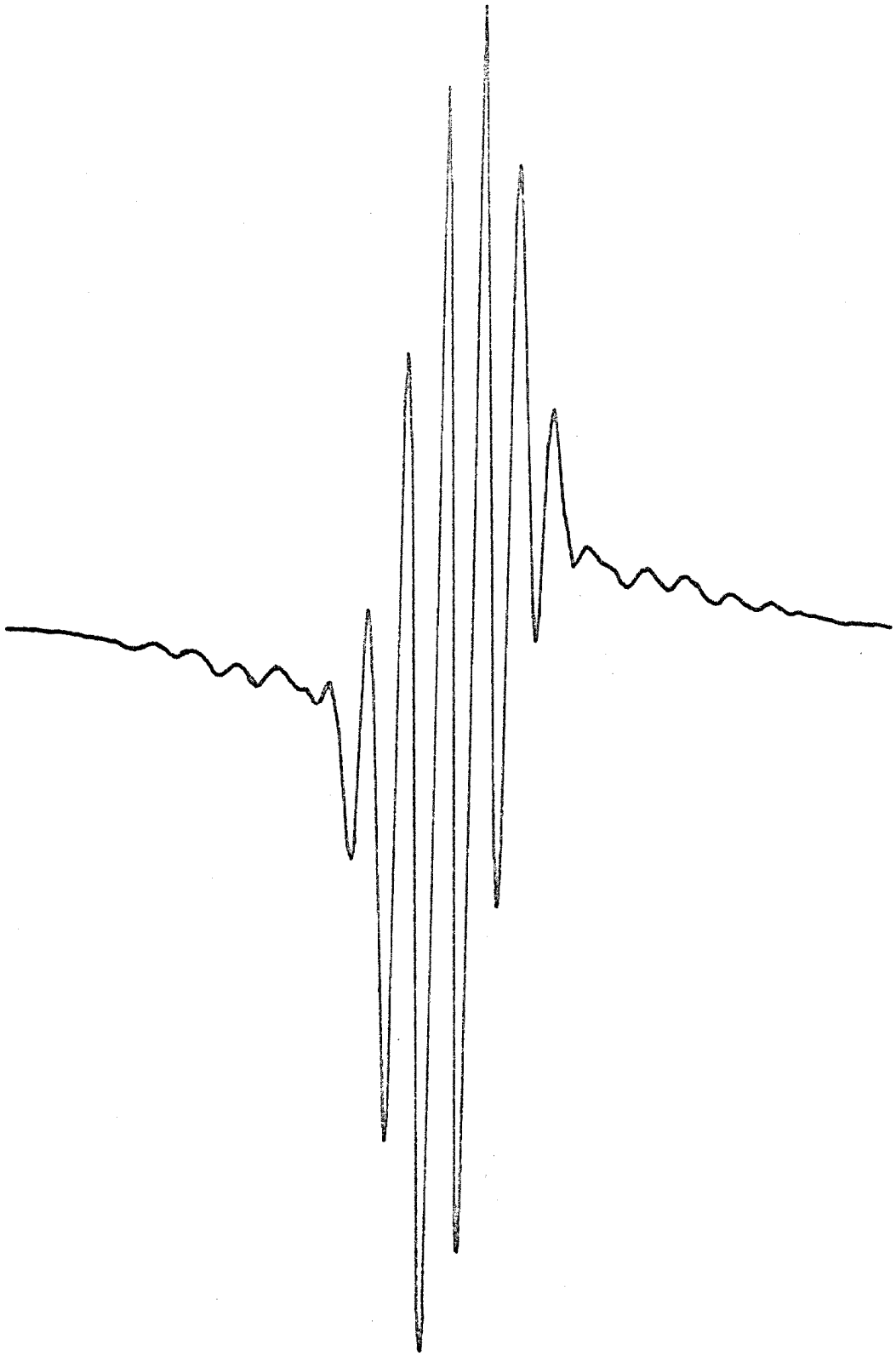


FIGURE 12. CHT-thiourea showing methanol impurity.

period of a few hours. A few hexagonal needles usually grow from the pointed bottom of the tube. Sometimes well developed crystals with dimensions of 1 x 10 mm will be formed.

Irradiation with 32 milliamp, 50 kilovolt, tungsten x-rays at a distance of 4 cm from the target produces CHT radicals rapidly, up to a maximum concentration, in approximately 15 minutes; thereafter, further irradiation begins to produce an impurity with a broad unresolved ESR absorption which increases to the size of the CHT absorption if the sample is irradiated a few hours. UV irradiation produces no CHT at room temperature; however, there is some formation of CHT when irradiation takes place at 77°K.

Even though the crystals are stable for months when left in the mother liquor, they should be irradiated and used as soon as possible after their removal from it. One day after irradiation the CHT absorption will fall by 100 times while the impurity radicals remain the same. Irradiation again will increase the CHT absorption but only to 1/10th of its previous value. Crystals which are irradiated the day after removal from the mother liquor give only 1/10th the CHT absorption that they would have given if irradiated immediately.

For low-temperature experiments, the crystals are attached to the crystal mount* with Kwiram Glue (page 8) and

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*See Part IIA of this thesis.

then coated entirely with it. This is necessary in order to keep the brittle crystals from breaking and falling off of the mount.

Experimental Results

For temperatures between 40° and 300°K the ESR spectrum consists of the characteristic eight equally spaced lines of CHT. This high-temperature spectrum is only slightly anisotropic, as can be seen in Table III. The C^{13} splittings for carbon in natural abundance were not observed. The explanation of the orientation is given in Fig. 13. Cooling the crystal from 300° to 40°K results only in broader lines (Fig. 14), a slightly larger hyperfine splitting, and a small change in the g values.

In a temperature range of two or three degrees near 40°K, a dramatic change occurs in the hyperfine structure (Figs. 15,16). This low temperature spectrum is highly anisotropic and does not change further upon cooling the crystal to 4.2°K, excepting, of course, that it saturates with microwave power more readily at lower temperatures. This low temperature spectrum, like that of CHT-naphthalene, is not well resolved (Figs. 17-22). Table IV lists the features of the CHT-thiourea low temperature spectrum. The CHT-thiourea crystal structure requires that the ESR spectrum for $\theta = +X^{\circ}$ and $\theta = -X^{\circ}$ be the same and that the ESR spectrum have a $\pi/3$ period in θ. It requires also that the ESR spectrum for $\phi = X^{\circ}$ and $\phi = \pi - X^{\circ}$ be the same. Therefore, in the tables, $0 \leqslant \theta \leqslant \pi/6$ and $0 \leqslant \phi \leqslant \pi/2$. The outermost

lines were sometimes hidden in the wings as a result of poor resolution; therefore, some weak lines are undoubtedly missing from Table IV.

TABLE III. Cycloheptatrienyl-Thiourea, High-Temperature Form

Temp.	Orientation ϕ	Orientation θ	hfs*	hfsx7	Line Width**	g Value***
300°K	0°	0°	3.72	26.1	1.53	2.0033
300	90	0	3.82	26.8	1.67	2.0030
300	90	30	3.82	26.8	1.67	2.0030
300	powder		3.77	26.4	1.60	2.0028
77	0°	0°	3.97	27.8	1.99	
77	7.5	0	3.97	27.8	2.12	2.0044
77	37.5	0	3.96	27.7	1.97	2.0037
77	90	0	4.05	28.4	2.02	2.0031
45	0	0	4.02	28.1	2.70	
45	90	0	4.01	28.1	2.44	2.0027

*Hyperfine splitting (gauss).

**Full width between maximum slope and minimum slope (gauss).

***Polycrystalline diphenyl picryl hydrazyl (13) and peroxylamine disulfonate ion (17) were used as internal standards and the absolute value of the g values should be correct to ±.0004 while relative values should be correct to ±.0001.

TABLE IV. Cycloheptatrienyl-Thiourea, Low-Temperature Form

ϕ	θ	First (low-field) point of max. slope to the successive points of max. slope (1st row) and to the points of min. slope (2nd row) of the ESR absorption curve (gauss)													First point (0.0) to point of zero slope (gauss)	g Value*
0°	0°	0.0	2.7	5.8	8.9	11.6	14.2	17.6	21.0	24.8	. .	. .	. .	. .	. .	12.3	. . .
		0.8	4.1	7.5	10.9	13.3	16.3	19.3	22.5	25.8	. .	. .	. .	. .	. .		
7.5	0	0.0	2.8	5.8	9.3	12.2	15.1	18.9	22.3	25.5	. .	. .	. .	. .	. .	12.9	2.0027
		1.0	4.4	7.7	11.5	14.5	17.4	21.1	24.0	26.8	. .	. .	. .	. .	. .		
17.5	0	0.0	2.6	5.5	9.2	12.3	15.4	19.0	21.7	25.7	. .	. .	. .	. .	. .	10.9	2.0038
		0.9	4.5	8.0	11.5	14.9	17.8	21.0	24.1	26.3	. .	. .	. .	. .	. .		
27.5	0	0.0	2.8	5.9	9.8	13.8	16.9	. .	. .	. .	. .	. .	. .	. .	. .	11.4	2.0037
		0.7	4.9	8.7	12.4	16.5	24.2	. .	. .	. .	. .	. .	. .	. .	. .		
37.5	0	0.0	2.8	5.9	10.8	14.1	16.7	19.2	22.5	25.9	. .	. .	. .	. .	. .	11.8	2.0036
		0.9	4.4	9.6	12.8	16.2	19.0	21.5	24.0	26.7	. .	. .	. .	. .	. .		
47.5	0	0.0	2.9	6.0	8.8	11.7	14.5	17.1	20.1	23.0	26.8	. .	. .	. .	. .	12.6	2.0033
		1.0	4.6	7.9	10.5	13.4	16.2	18.9	22.1	24.7	27.7	. .	. .	. .	. .		
57.5	0	0.0	3.1	4.4	6.7	11.8	15.2	19.3	21.3	23.2	27.7	. .	. .	. .	. .	13.2	2.0032
		1.3	3.6	5.5	10.0	14.1	18.2	20.4	22.7	24.8	28.5	. .	. .	. .	. .		
67.5	0	0.0	4.3	6.9	11.5	13.9	15.8	18.9	21.0	27.1	30.9	. .	. .	. .	. .	12.7	2.0035
		1.5	5.2	10.5	13.5	15.2	18.5	19.9	23.7	27.8	31.6	. .	. .	. .	. .		
77.5	0	0.0	5.7	8.0	10.7	13.0	15.5	17.9	20.3	26.0	28.2	. .	. .	. .	. .	13.5	2.0028
		2.0	7.2	10.0	12.3	14.5	17.3	19.2	22.2	26.5	29.0	. .	. .	. .	. .		
82.5	0	0.0	2.0	6.0	7.9	12.1	14.0	17.5	20.4	23.7	27.0	29.9	32.5	. .	. .	15.0	2.0026
		0.8	3.6	6.6	10.3	13.0	16.4	18.5	22.9	24.4	28.3	31.1	33.2	. .	. .		
87.5	0	0.0	2.1	6.0	8.1	11.6	13.9	17.3	20.2	23.4	26.8	29.6	. .	. .	. .	14.7	2.0027
		0.7	3.6	6.4	10.4	12.9	16.0	18.9	22.6	24.6	28.0	30.8	. .	. .	. .		
90	0	0.0	2.7	5.2	8.7	11.1	14.5	17.4	20.4	23.8	26.5	30.1	33.0	36.0	. .	18.4	2.0032
		0.9	3.7	6.7	10.0	12.9	16.2	19.2	22.1	25.5	28.1	31.3	34.4	36.6	. .		
90	5	0.0	2.6	5.2	8.9	11.2	14.9	17.6	20.8	23.9	26.7	30.4	33.1	36.3	. .	18.3	. . .
		1.0	3.8	6.8	10.1	13.0	16.5	19.4	22.2	25.6	28.3	31.7	34.6	37.0	. .		
90	10	0.0	2.9	5.6	9.3	11.5	15.3	18.0	21.1	24.0	27.0	31.0	33.5	36.6	. .	18.8	. . .
		1.4	4.2	7.1	10.5	13.5	16.8	12.0	22.7	26.0	28.7	32.0	34.9	37.2	. .		
90	15	0.0	2.7	5.0	8.7	10.7	15.1	17.4	20.7	23.9	26.5	30.9	33.1	36.5	. .	18.5	2.0042
		0.8	3.7	6.6	9.8	13.2	16.5	19.6	22.3	25.9	28.4	31.8	34.7	37.5	. .		
90	20	0.0	2.7	5.0	8.8	10.0	15.2	17.3	20.4	23.3	30.8	33.1	36.1	. .	. .	18.3	. . .
		0.8	3.8	6.4	9.4	13.8	16.6	19.5	22.0	28.4	31.8	34.7	37.0	. .	. .		
90	25	0.0	2.9	5.2	10.2	15.6	20.6	24.7	31.2	33.4	36.6	. .	. .	. .	. .	18.2	. . .
		1.0	4.0	6.7	14.2	20.3	22.5	28.7	32.0	34.7	37.2	. .	. .	. .	. .		
90	30	0.0	2.9	5.4	10.6	12.9	15.9	17.8	20.7	23.7	25.7	28.4	31.6	33.8	36.9	19.3	. . .
		0.5	3.9	6.8	12.5	14.5	17.5	20.0	22.3	24.9	27.7	29.0	32.4	35.3	37.8		
powder		Peak to peak width 35 gauss. At least 4 poorly resolved lines.									. .	. .	. .	. .	. .	. .	2.0023

*Peroxylamine disulfonate ion (17) was used as an internal standard. The absolute value of the g values should be correct to ±.0004, the relative values should be correct to ±.0002.

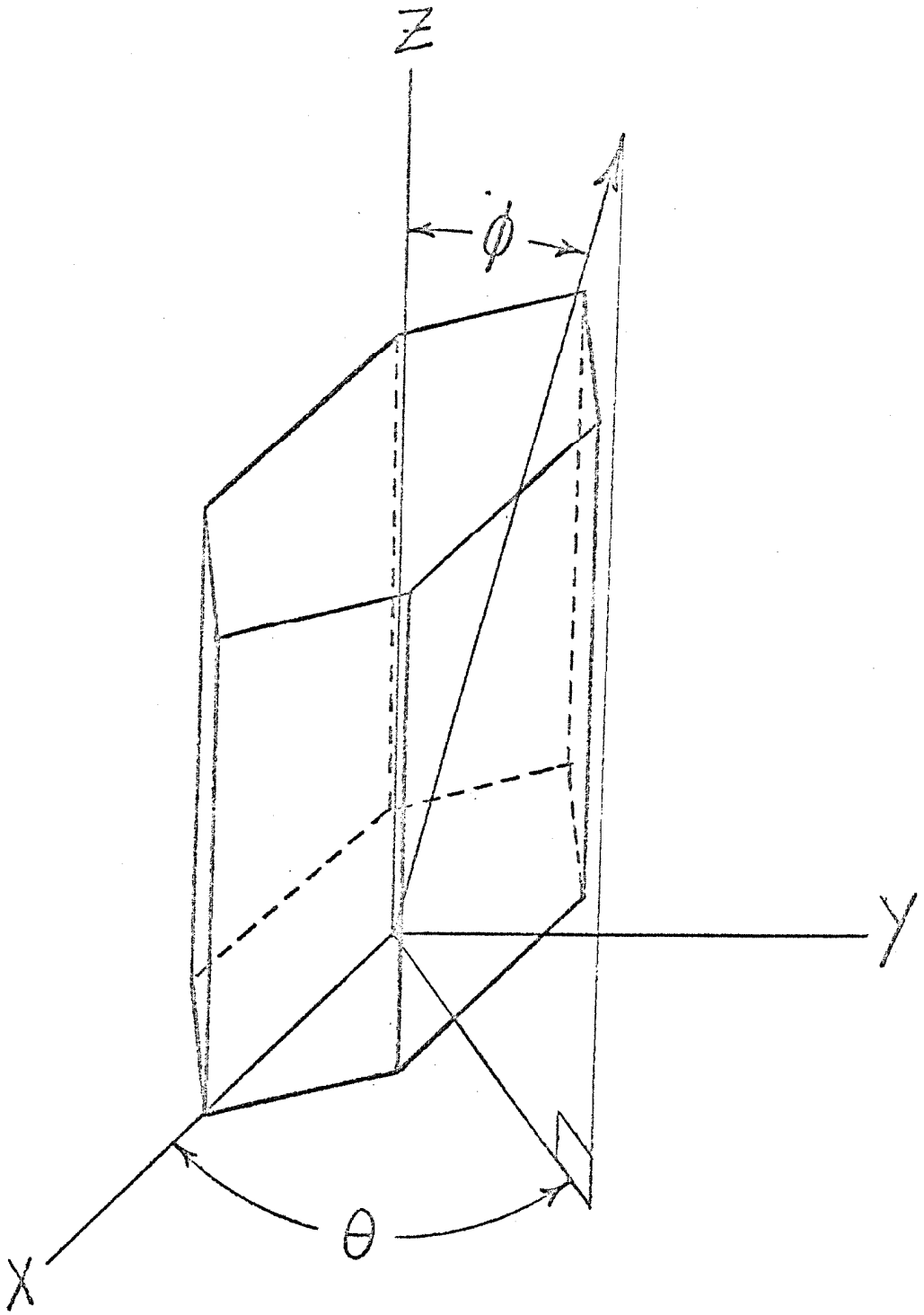

FIGURE 13. Definition of angles for CHT-thiourea crystals.

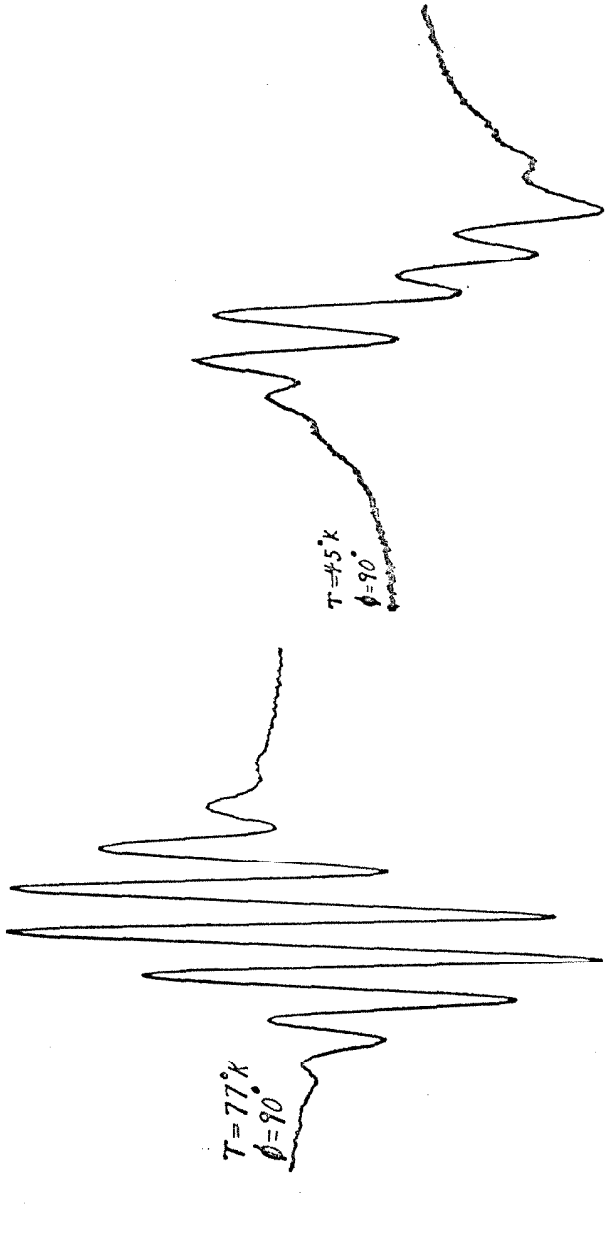

FIGURE 14. Broadening of CHT-thiourea upon cooling.

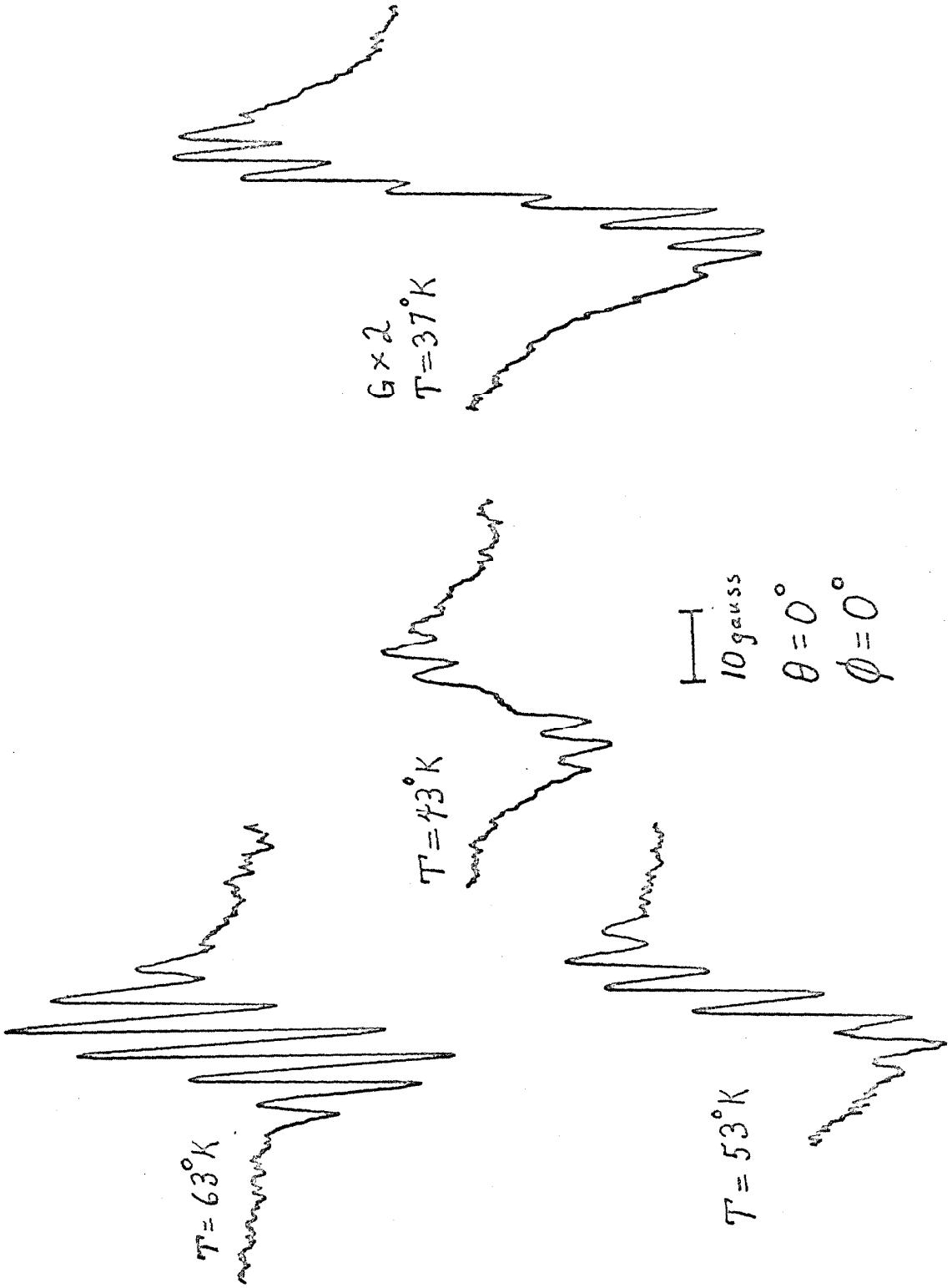

FIGURE 15. Transition of CHT-thiourea. $\phi = 0°$.

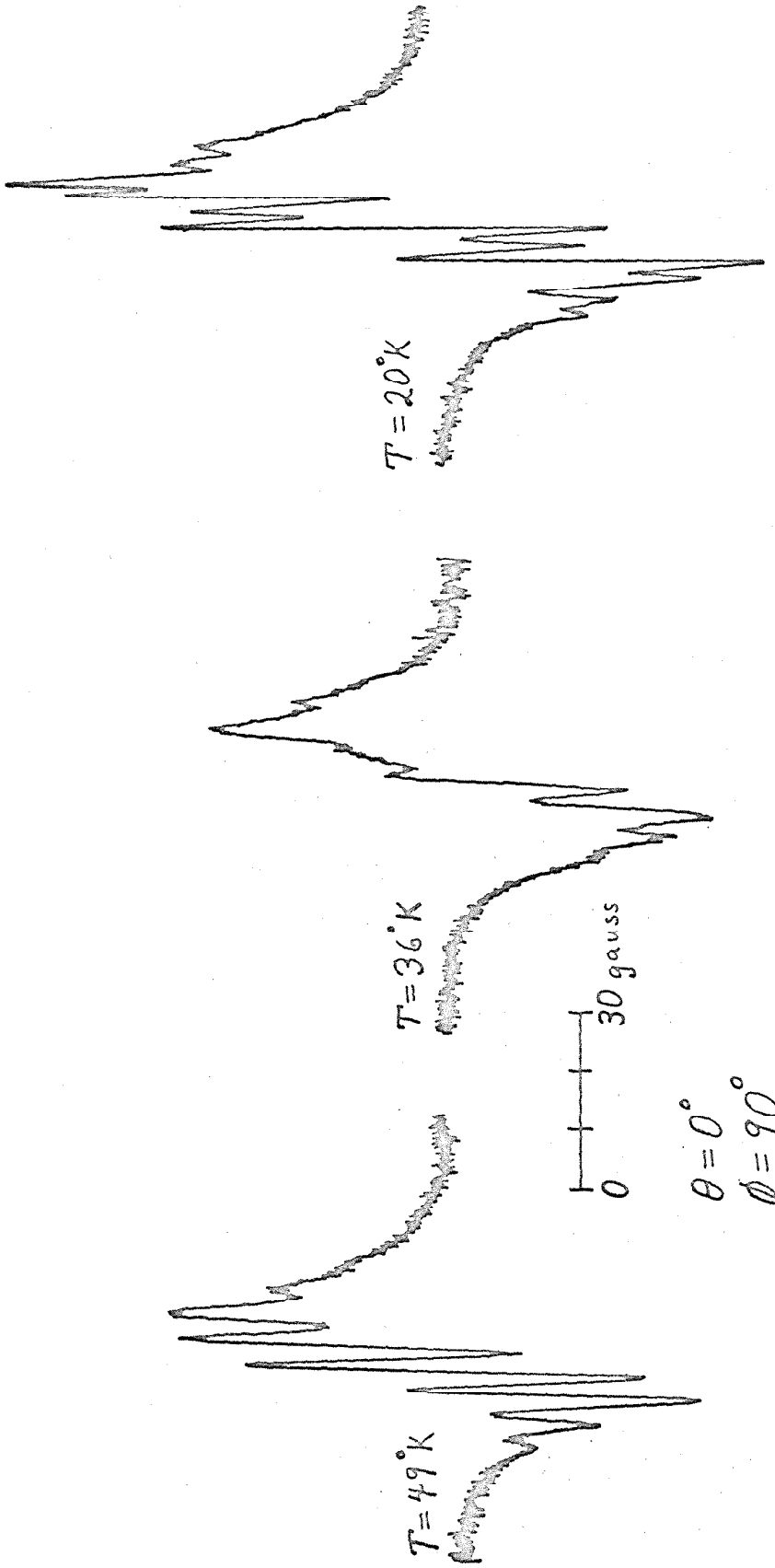

FIGURE 16. Transition of CHT-thiourea. $\phi = 90°$.

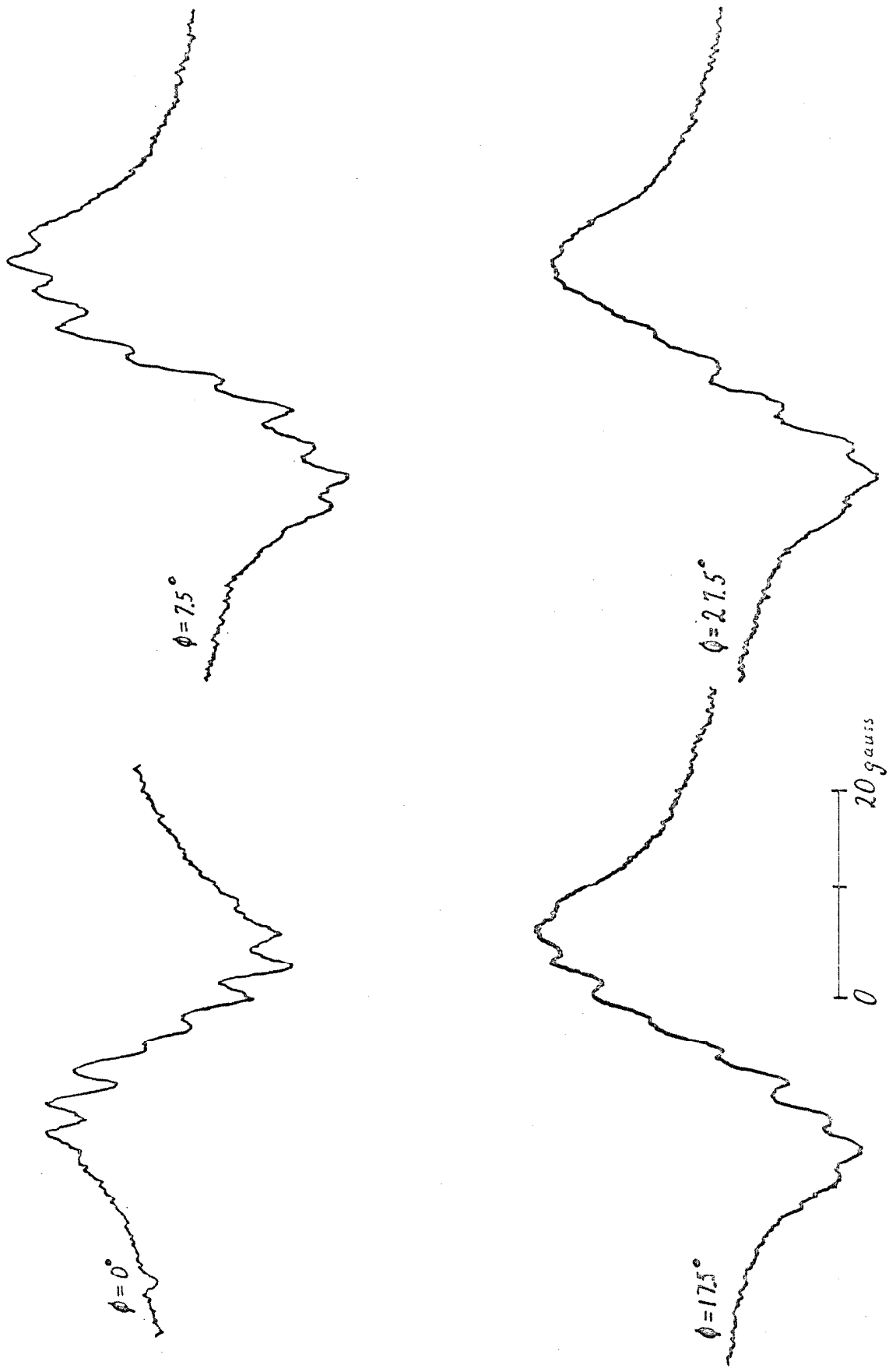

FIGURE 17. Low-temperature spectra of CHT-thiourea.

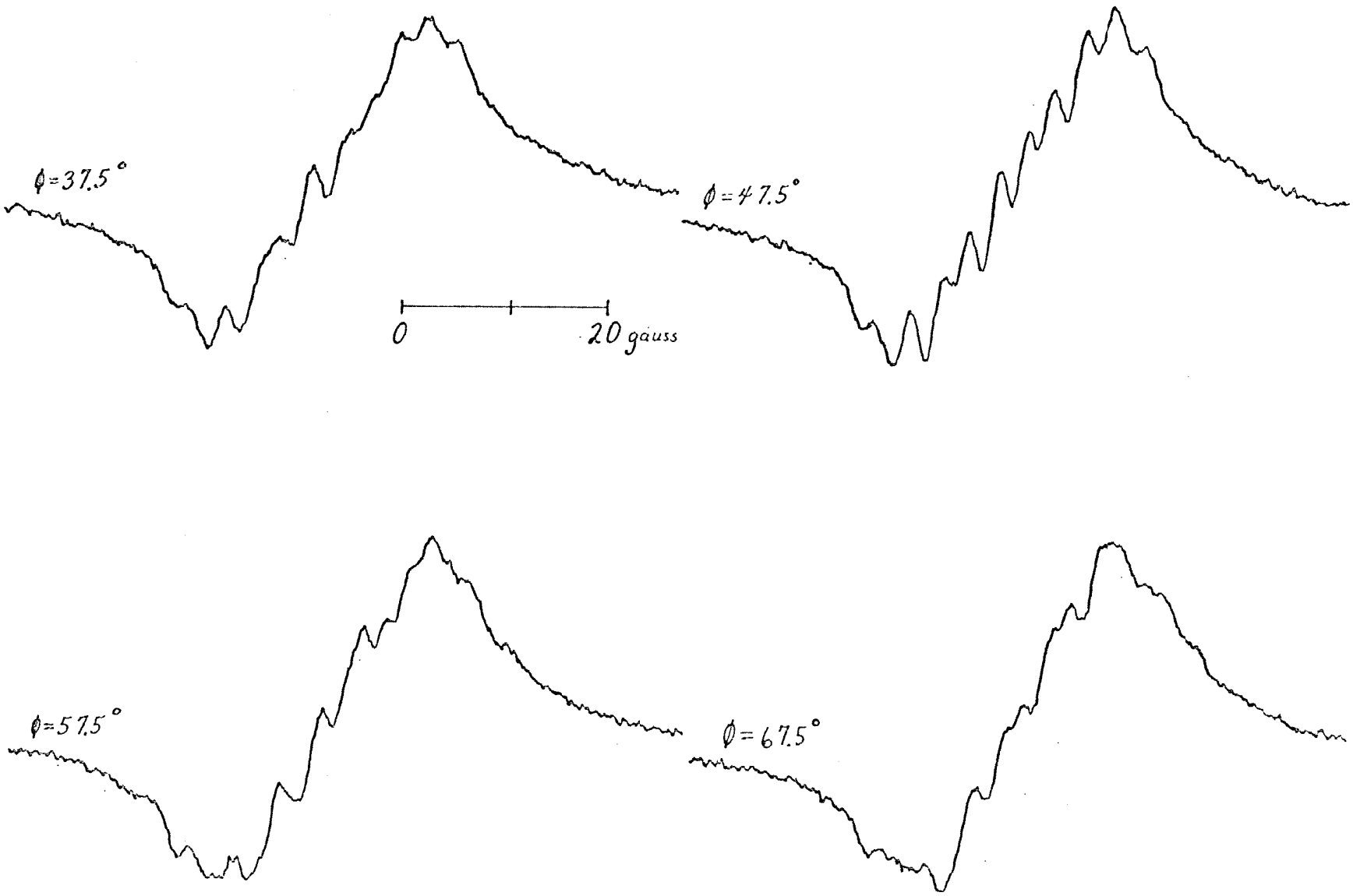

FIGURE 18. Low-temperature spectra of CHT-thiourea.

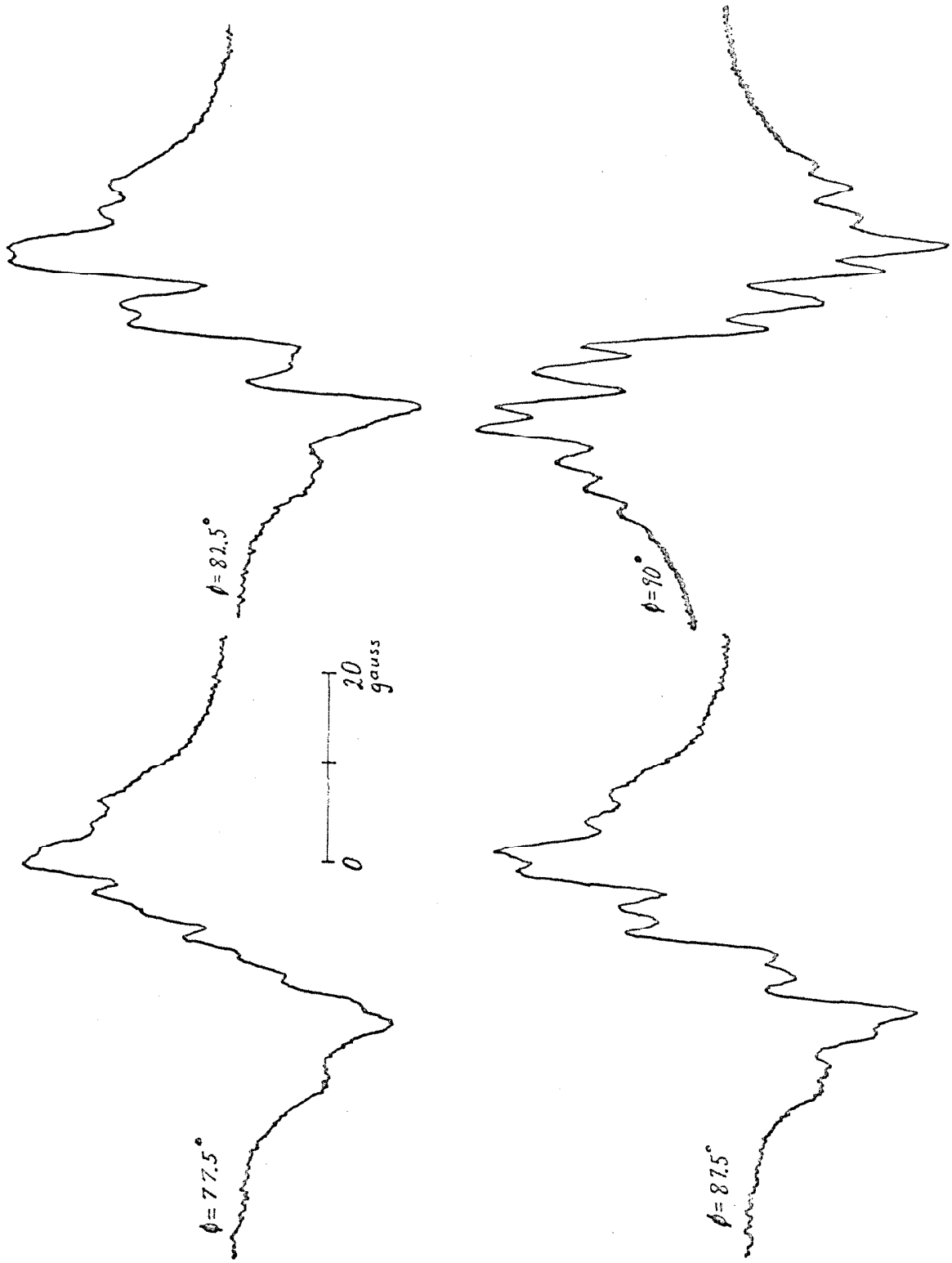

FIGURE 19. Low-temperature spectra of CHT-thiourea.

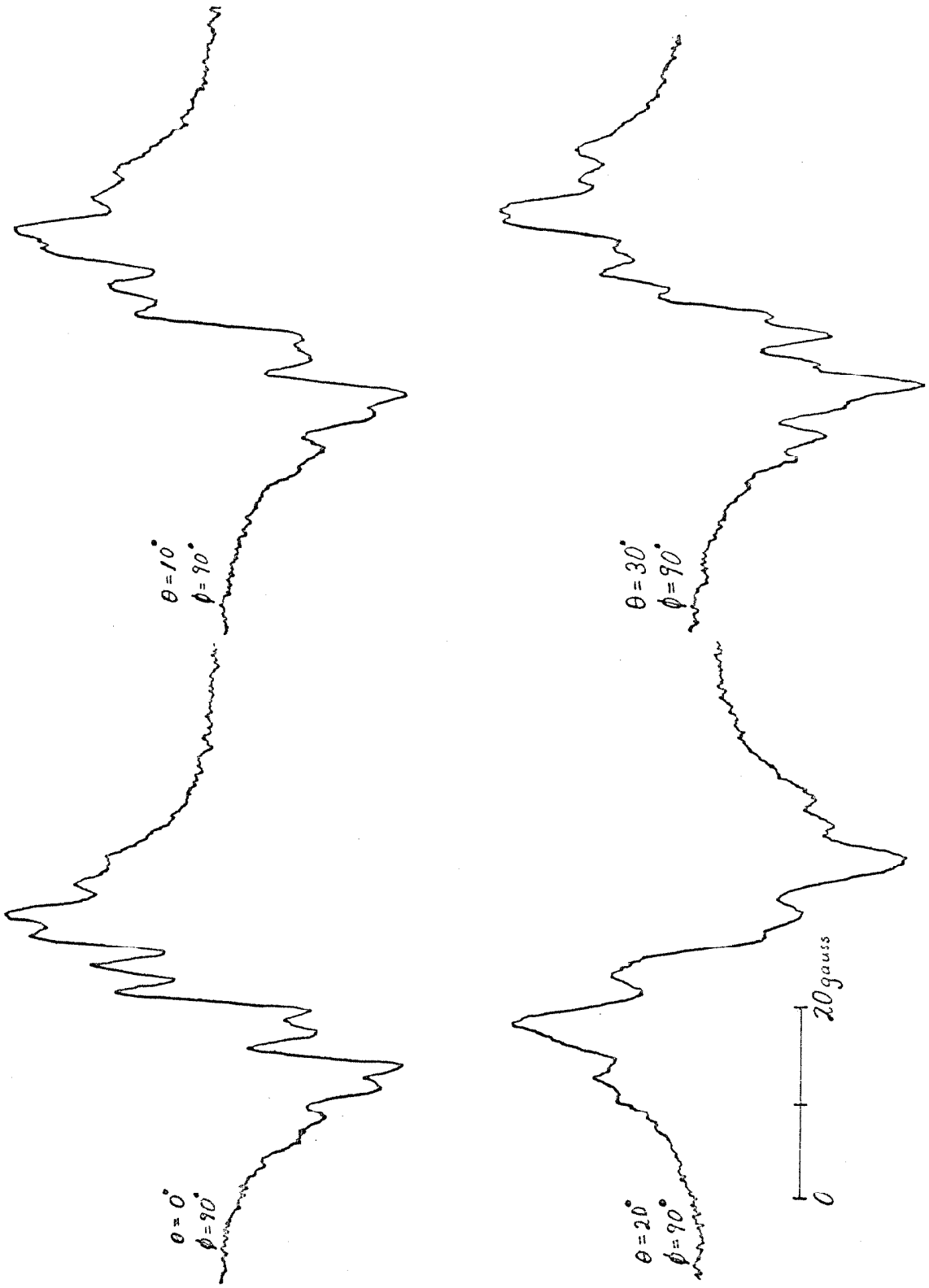

FIGURE 20. Low-temperature spectra of CHT-thiourea.

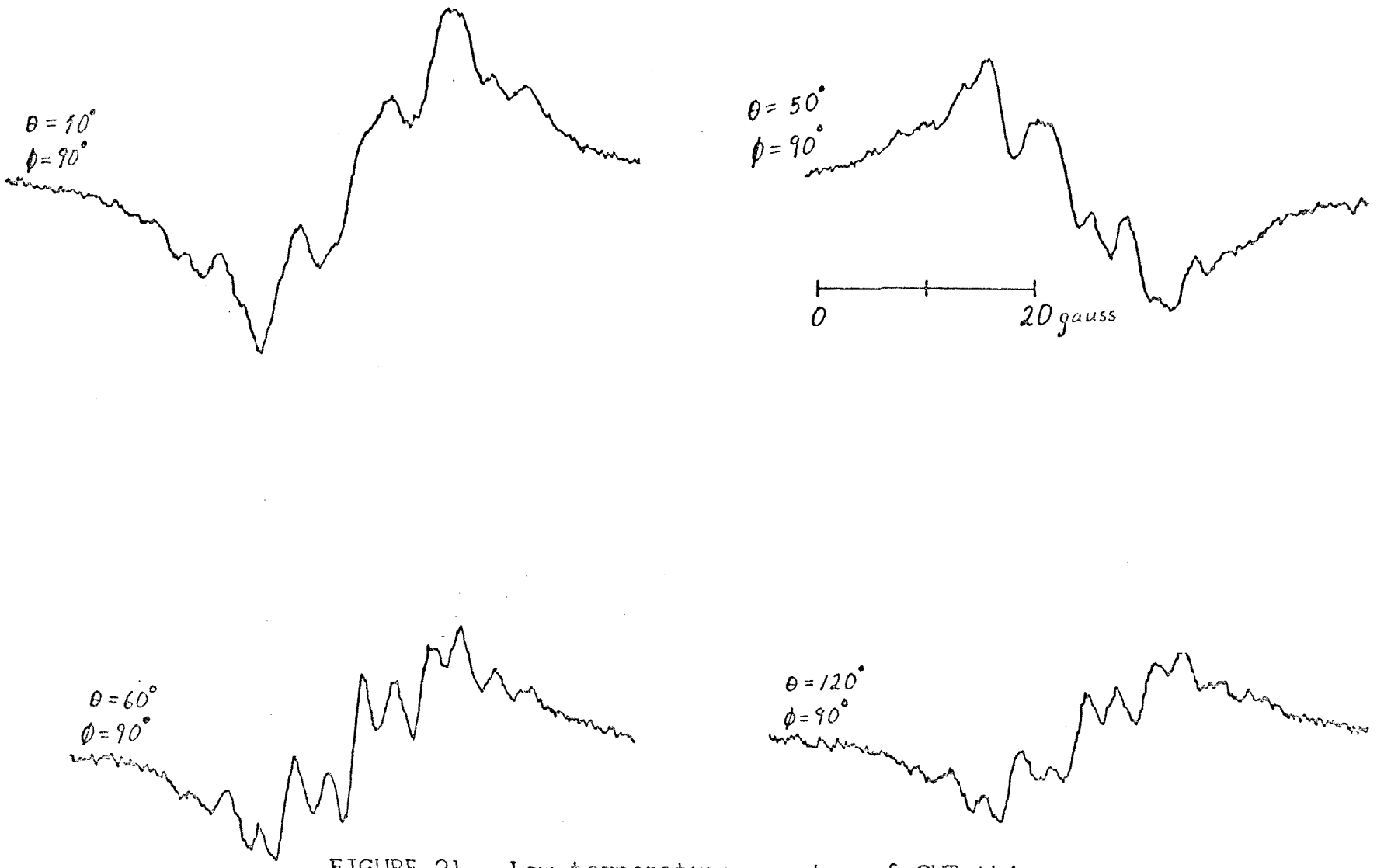

FIGURE 21. Low-temperature spectra of CHT-thiourea.

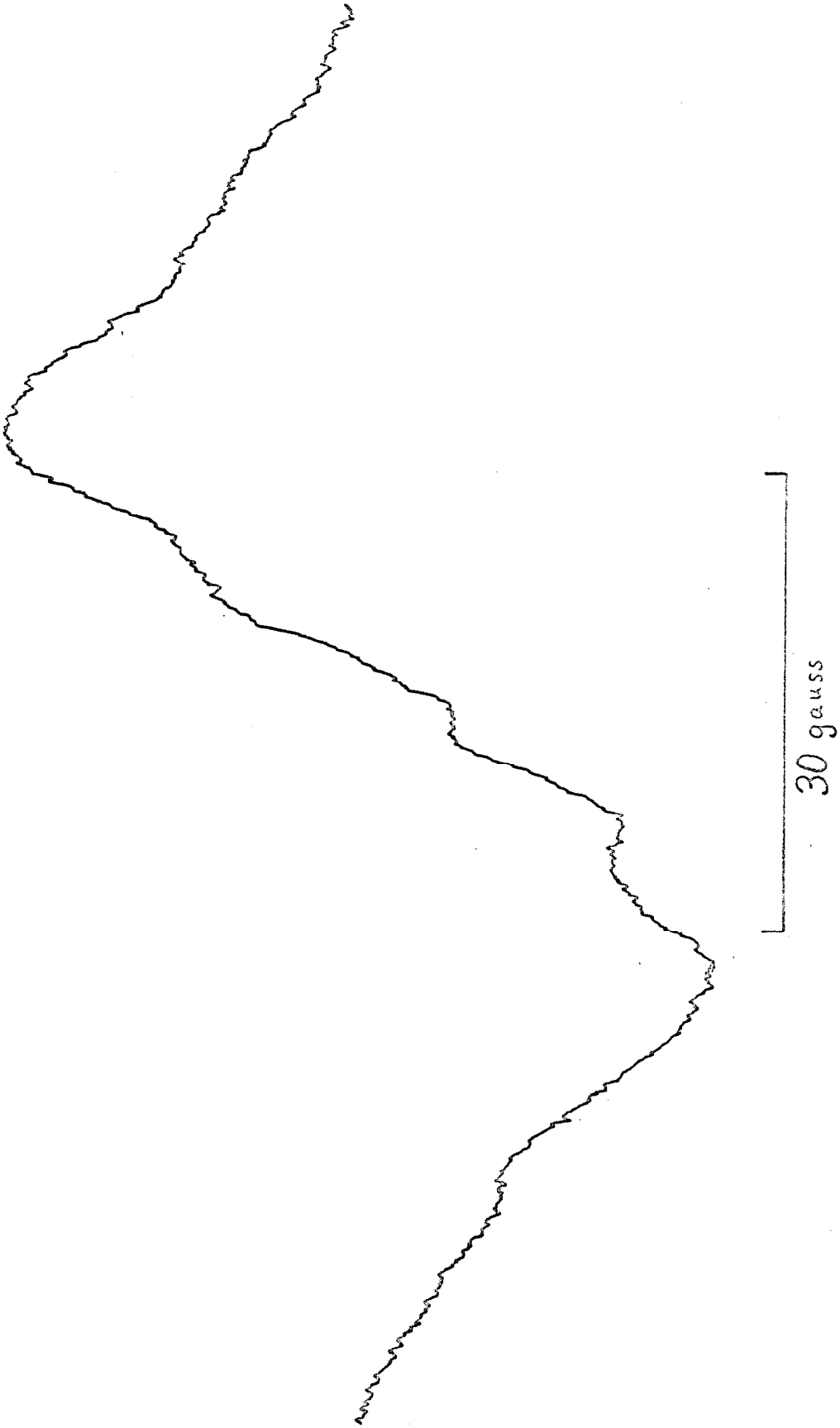

FIGURE 22. Low-temperature spectrum of CHT-thiourea powder.

D. CYCLOHEPTATRIENYL-CYCLOHEPTATRIENE

Preparation of Samples

A moderate concentration of CHT radicals in a polycrystalline cycloheptatriene matrix was obtained by the vapor-phase photolysis of cycloheptatriene.

The gas deposition apparatus (Fig. 23) is designed to be used with the dewar built by A. Kwiram (18). A bulb containing cycloheptatriene is kept at 0°C, where its vapor pressure is approximately 20 mm Hg. The quartz capillary is constricted in two places to give a flow rate of 2 STP ml/min with a pressure differential of 20 mm Hg. An Osram HBO 100 W/1 mercury super-pressure lamp irradiates the vapor in the tip of the quartz capillary, and a General Electric BH-6 high-pressure mercury capillary lamp irradiates the vapor after it leaves the capillary. The vapor is then immediately deposited on the quartz cold finger, which is cooled either by cold helium gas or by liquid helium or by liquid nitrogen. The usual deposition time was ten minutes. A copper-constantan thermocouple was inserted into the cold finger in order to measure its temperature.

Reed and Lipscomb (19) studied the crystal structure of cycloheptatriene (mp 193°K). They found a highly disordered cubic phase, $a = 10.6 \pm .1$ Å, of O_h symmetry. But a major transition at approximately 148°K turns the crystal into a powder; therefore, the crystal structure below this temperature is completely unknown.

Experimental Results

The usual eight-line high-temperature spectrum of the deposited CHT is observed between 10° and 77°K (Fig. 24). An additional, broad (~100 gauss) resonance is also observed. However, ultraviolet light shined directly upon the deposit destroys the free radical responsible for this extraneous signal. The CHT spectrum broadens as the deposit is cooled from 77° to 10°K, as can be seen in Table V and in Fig. 24.

The change* to the low-temperature spectrum occurs at 10°K ±2°(Fig. 24). The g value of the low-temperature spectrum is 1.9985 which, compared to most hydrocarbon free radicals, is remarkably low. The features of the spectrum at 4.2°K are listed in Table VI.

*The actual transition temperature may be somewhat higher than measured (with a thermocouple inside the cold finger) because room-temperature radiation was striking the deposit.

TABLE V. Cycloheptatrienyl in Cycloheptatriene (Polycrystalline), High-temperature Form

Temp.	hfs*	hfsx7	Line Width**	g Value
77°K	3.97	27.8	2.03	2.0028 abs. ±.0004 rel. ±.0001
61	3.97	27.8	2.03	
49	4.00	28.0	2.07	
35	4.00	28.0	2.14	
15	4.00	28.0	2.15	

*Hyperfine splitting (gauss).

**Full width between maximum and minimum slope (gauss).

TABLE VI. Cycloheptatrienyl in Cycloheptatriene (Polycrystalline), Low-temperature Form

First (low-field) point of maximum slope to the successive points of maximum slope (first row) and to the points of minimum slope (second row) of the ESR absorption curve (gauss)						First point (0.0) to point of zero slope (gauss)	g Value
0.0	4.4	7.1	11.6	20.5	28.5	17.4	1.9985 +.0015 -.0003
2.0	5.4	9.5	18.9	26.2	31.1		

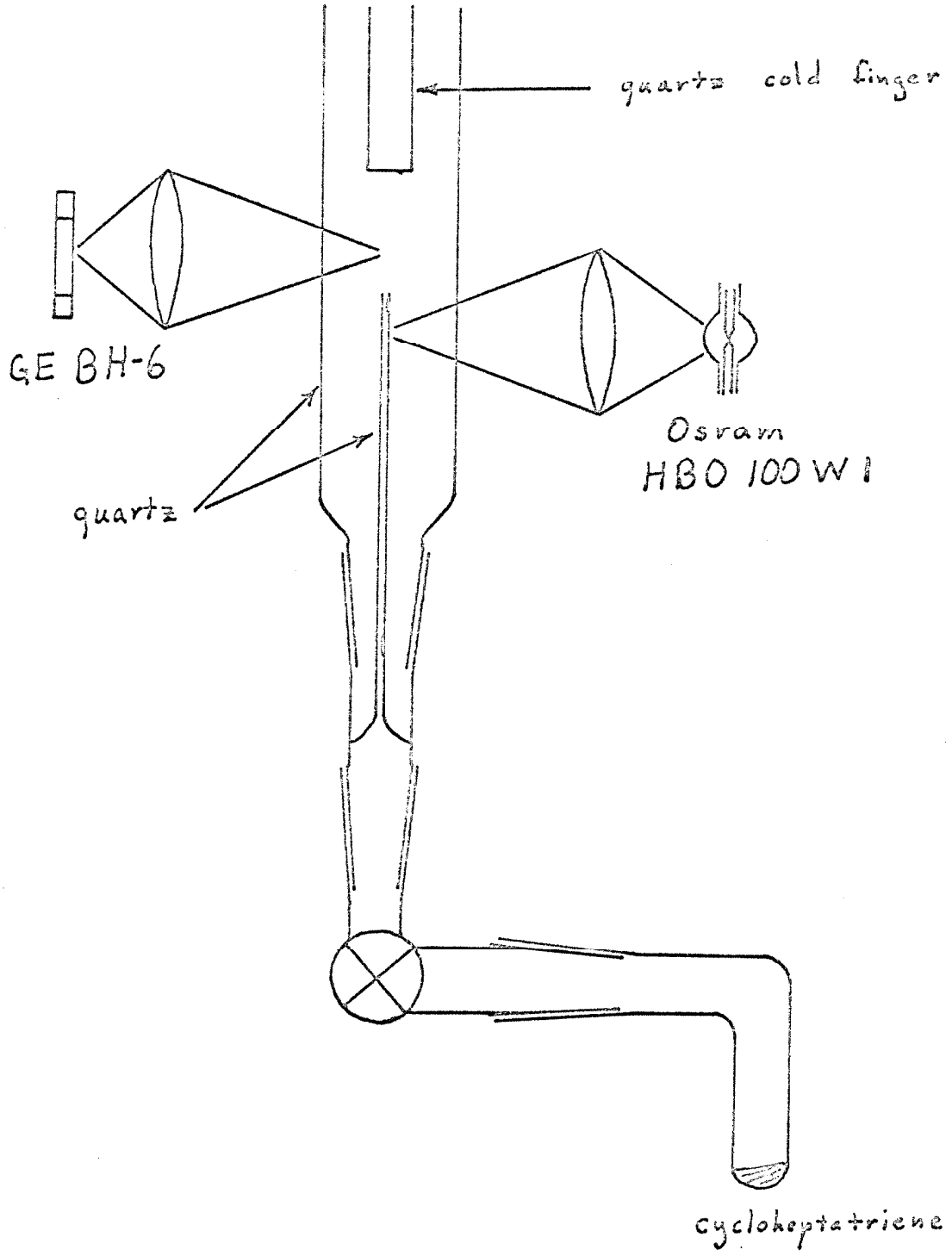

FIGURE 23. Gas deposition apparatus for CHT-cycloheptatriene.

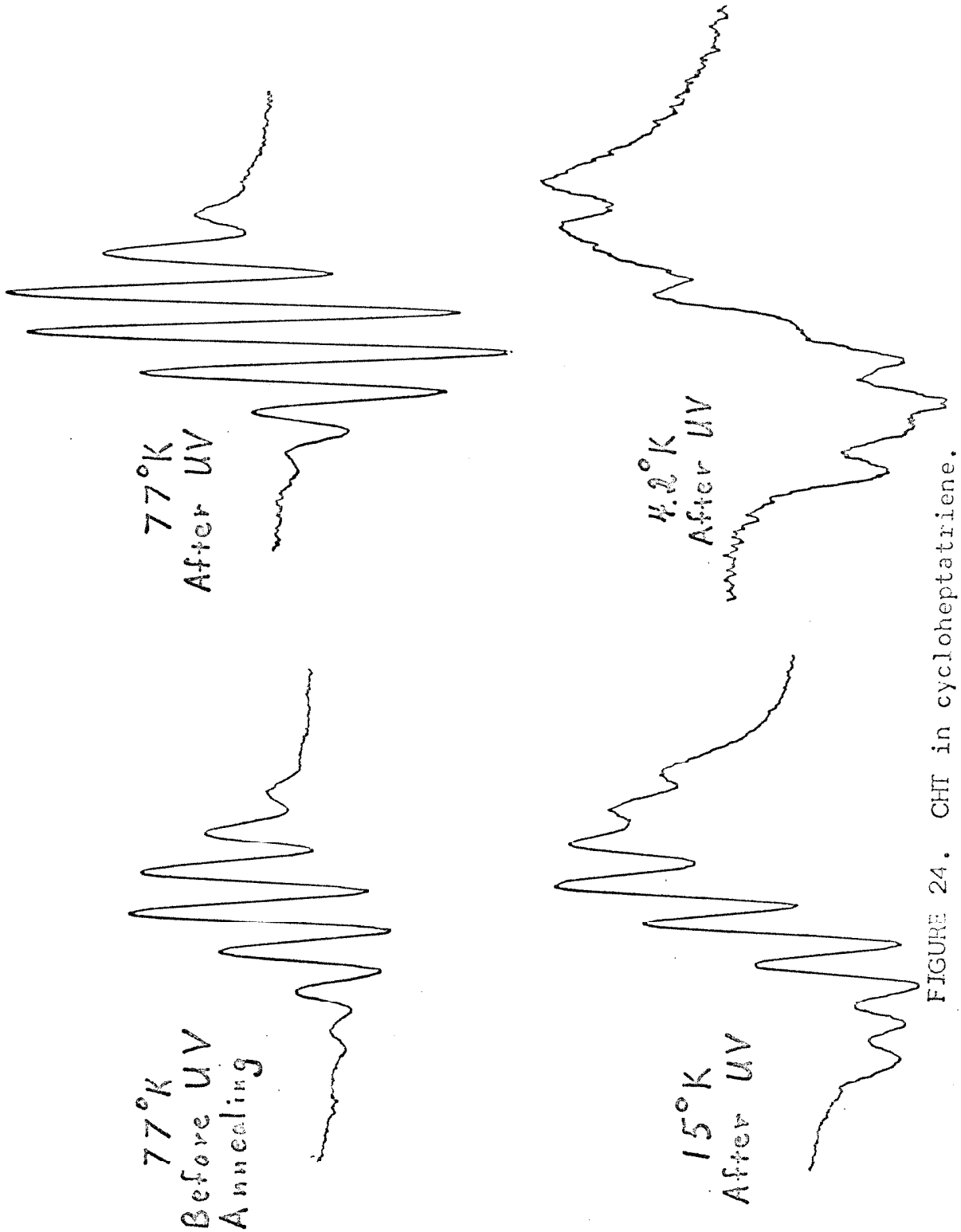

FIGURE 24. CHT in cycloheptatriene.

E. CYCLOHEPTATRIENYL-ARGON

Preparation of Samples

A moderate concentration of CHT radicals in a solid argon matrix was obtained by the vapor-phase photolysis of (a) cycloheptatriene or (b) bitropyl*, followed by co-condensation with argon. Both (a) and (b) gave identical results. The photolysis produces no radicals in the presence of argon gas. The hydrocarbons are apparently deactivated by collision with argon before bond breakage can occur.

The gas deposition apparatus is depicted in Fig. 25. Cycloheptatriene at -110°C or bitropyl at 30°C (where their vapor pressure is approximately 0.1 mm Hg) is kept in a pyrex bulb. The quartz capillary admitting the hydrocarbon is constricted in two places to give a flow rate of 0.5 STP ml/min with a pressure differential of 15 mm Hg. An Osram HBO 100 W/1 mercury super-pressure lamp irradiates the vapor in the tip of the quartz capillary, and a General Electric BH-6 high-pressure mercury capillary lamp irradiates the vapor after it leaves the capillary. The photolyzed gas stream travels 15 mm before the argon is added. The capillary admitting the argon is calibrated to deliver 0.5 STP ml/min with one atmosphere pressure-differential. The mixed gases are immediately deposited on

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*Bitropyl, $(C_7H_7)_2$, was prepared from cycloheptatriene according to the method of Doering and Knox (20) and was further purified by sublimation, yielding a colorless product of melting point 61.2 - 62.7°C.

the quartz cold finger, which is cooled by liquid helium. A deposition period of twenty minutes gave good results.

Experimental Results

The ESR spectrum of CHT in polycrystalline argon consists of two sets, differing only in g values, of eight equally spaced lines. Designate the radical with the lower g-value A and the radical with the higher g-value B. The relative amounts of A and B vary from preparation to preparation in an inconsistent manner. However, A was always present in at least twice the concentration of B. Ultraviolet light shined directly upon the solid deposit reduces the concentration of species B. Figures 26 through 28 show a sequence of decreasing A/B ratio. It seems probable that two types of lattice sites in the solid argon matrix are responsible for the two different g values observed for CHT: in one of these lattice sites, CHT may be substituting for two argon atoms, in the other, for three argon atoms.

The line widths of CHT in argon are approximately one-half of those in matrices containing protons. This is probably a result of dipolar broadening of the hyperfine levels of CHT by the protons in the surrounding matrix. The spectrum of CHT in argon is insensitive to temperature changes between 1.5° and 4.2°K. If there is a transition*

*The sample was exposed to room-temperature radiation and therefore may not have been as cold as the superfluid helium in the cold finger.

to a low temperature form, it must lie below 1.5°K. The same broad (~100 gauss) ESR absorption noted in Part IID (page 38) was present, and it could be removed, as before, by ultraviolet light shined upon the solid deposit. The important parameters of the CHT in Argon spectra are given in Table VII.

TABLE VII. Cycloheptatrienyl in Argon at 4.2°K

Radical	hfs (gauss)	hfsx7 (gauss)	Line Width* (gauss)	g Value**
A	3.94	27.6	1.06	2.0037
B***	3.94	27.6	1.06	2.0046

*Full width between points of maximum and minimum slope.

**Polycrystalline diphenyl picryl hydrazyl (13) was used as an internal standard. The absolute values should be correct to ±.0004 while the relative values should be correct to ±.0001.

***The values for B are not as accurate as those for A.

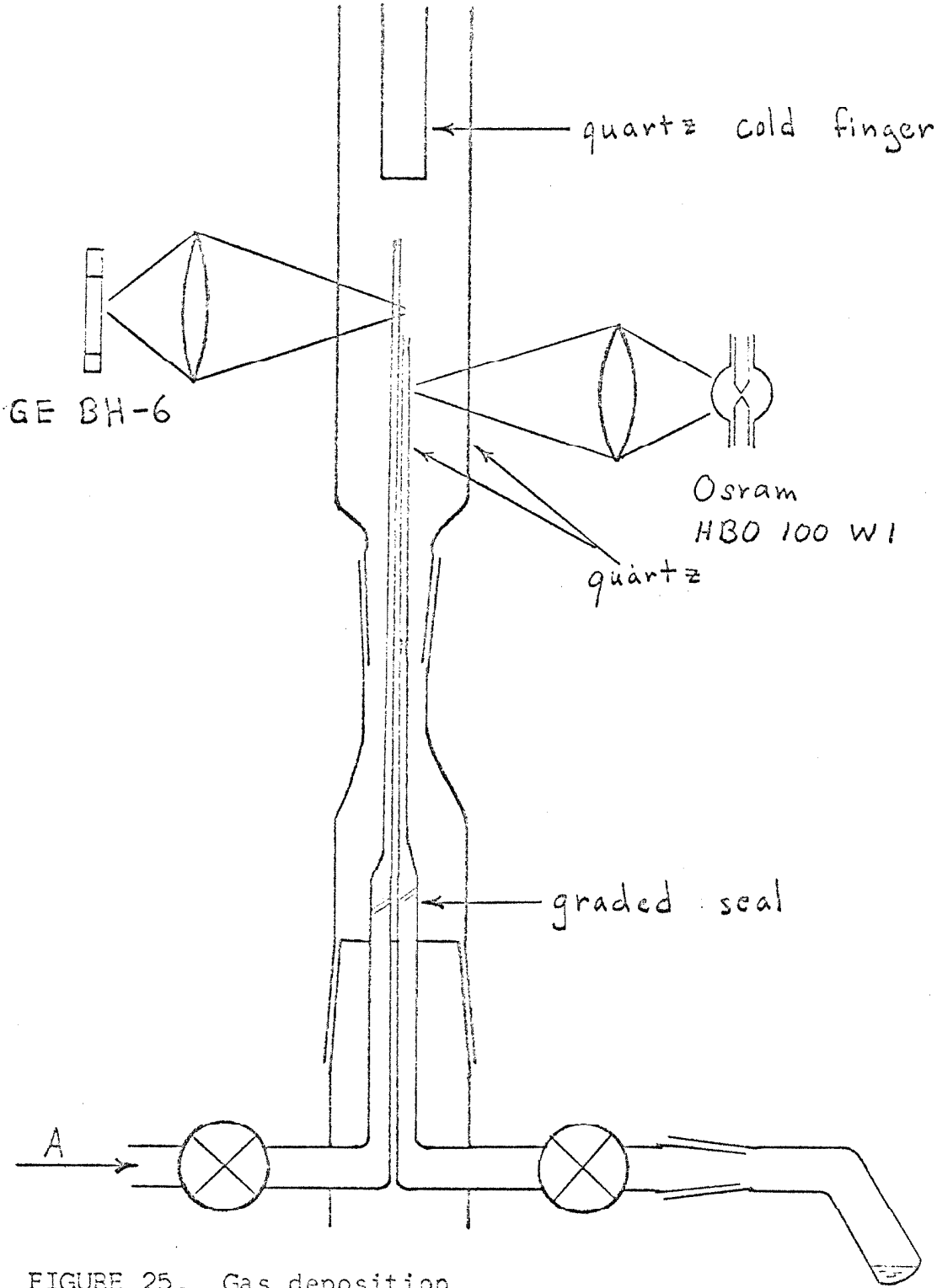


FIGURE 25. Gas deposition apparatus for CHT-argon.

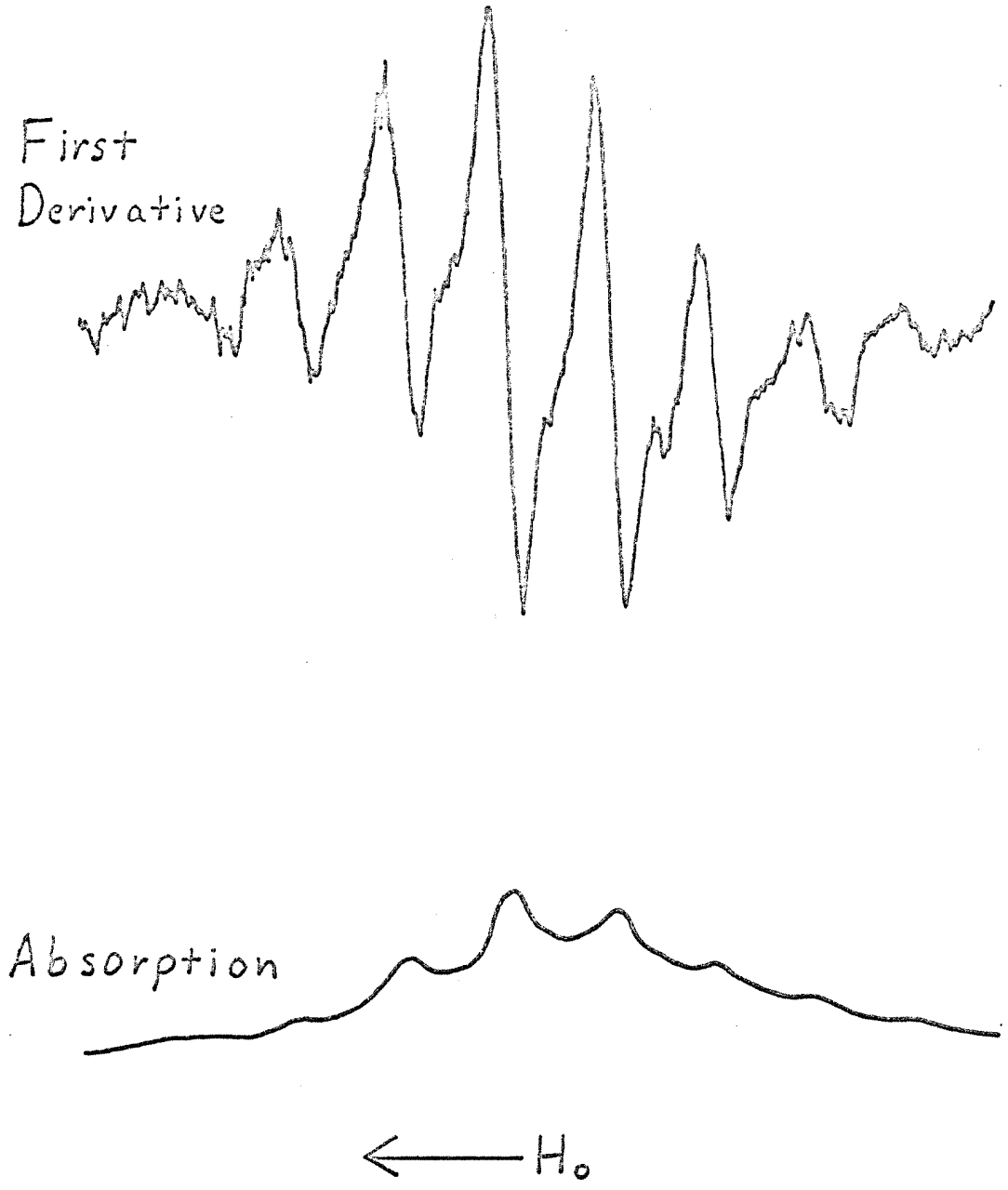


FIGURE 26. CHT in argon, A/B large, 4.2°K.

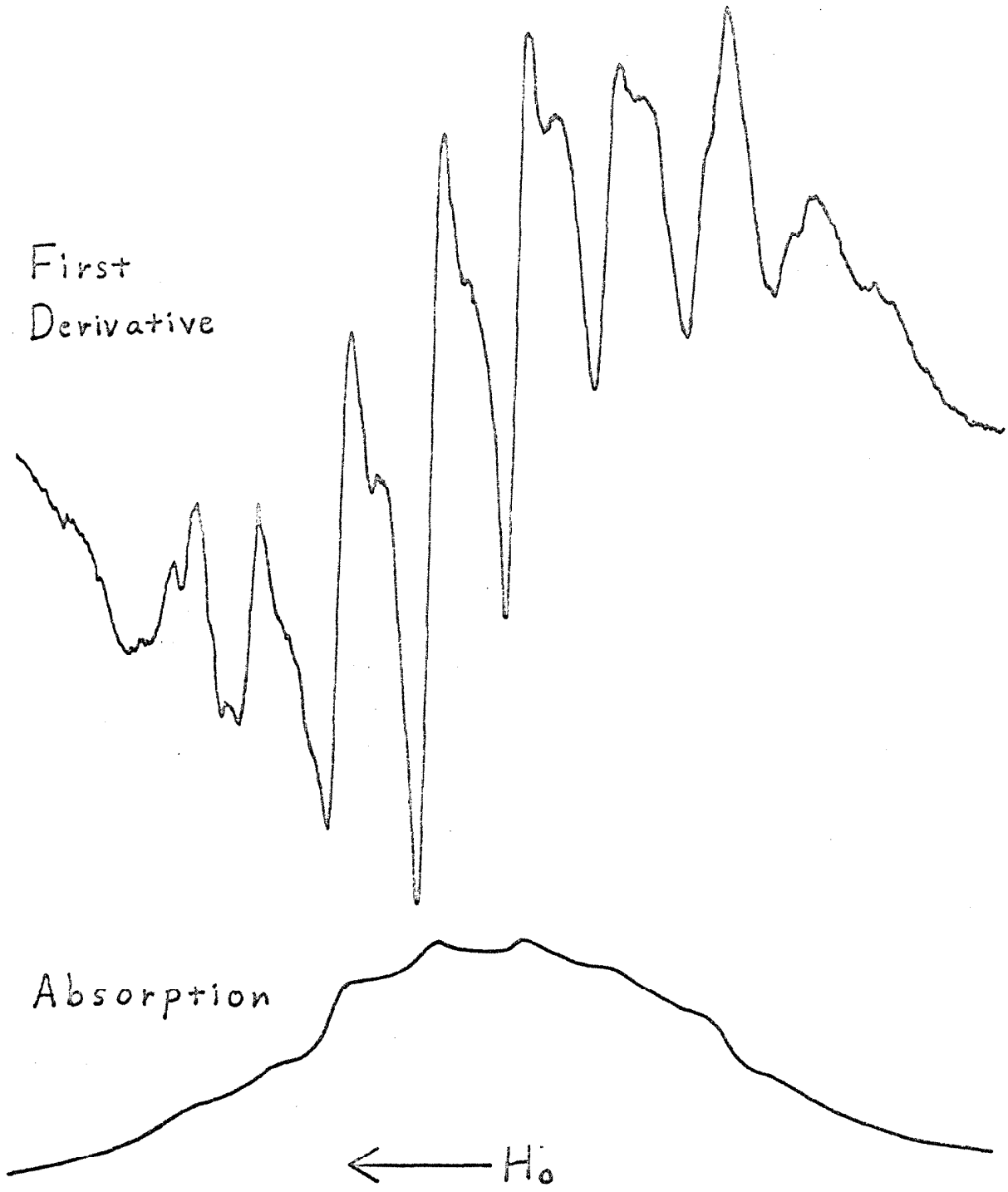


FIGURE 27. CHT in argon, A/B≈3, 4.2°K.

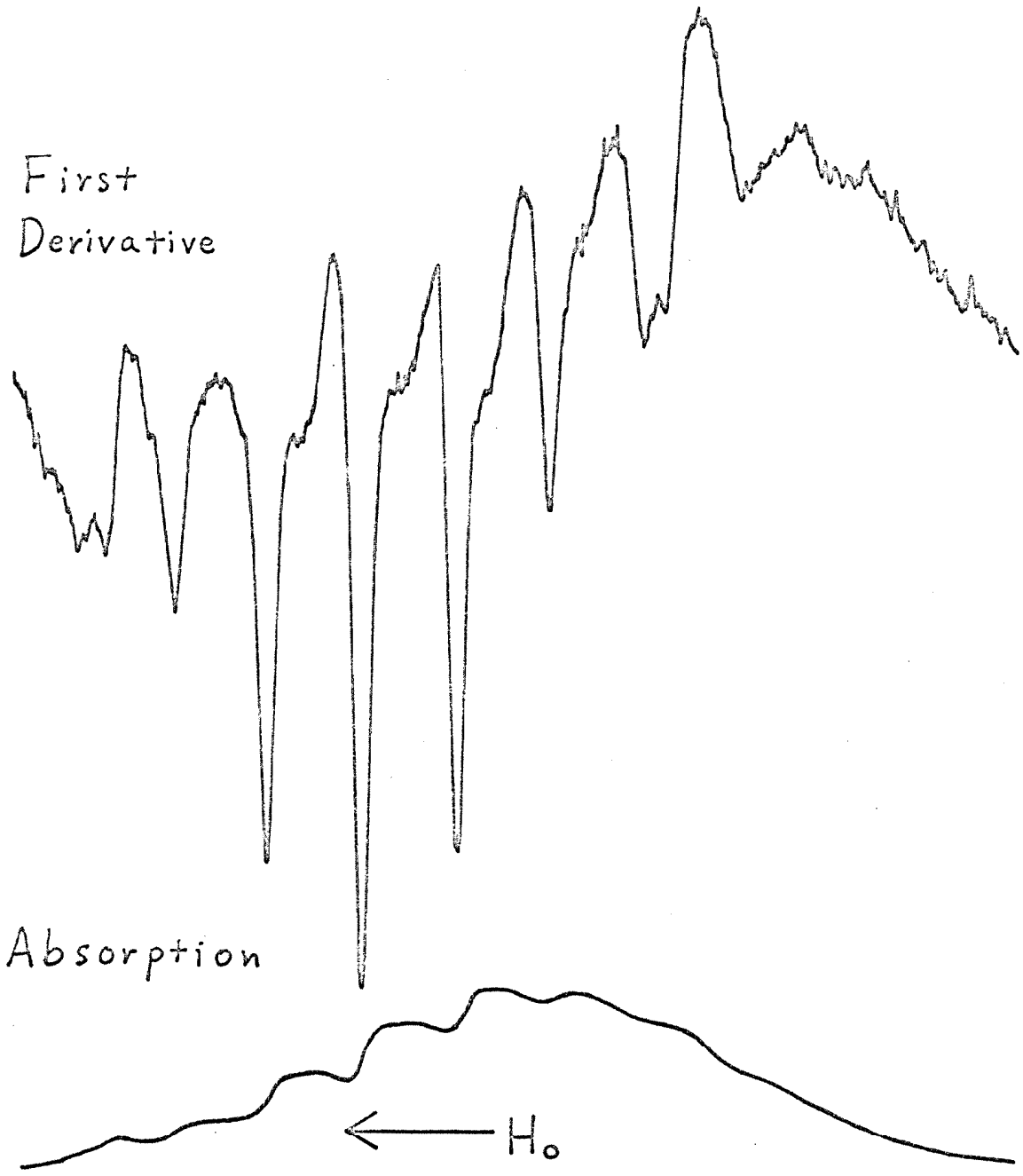


FIGURE 28. CHT in argon, A/B≈2, 4.2°K.

F. CYCLOHEPTATRIENE IN OTHER MATRICES

Many compounds were simply melted with cycloheptatriene, frozen, and then x-irradiated in order to find useful matrices for the ESR study of CHT. Table VIII summarizes the results of this study. Figure 29 shows two typical examples of positive results.

A durene single crystal doped with cycloheptatriene was irradiated with ultraviolet light at 77°K, but no CHT radicals were formed. A benzophenone crystal doped with cycloheptatriene, when treated in the same manner, gave a very strong ESR signal with a complicated hyperfine structure approximately 80 gauss in width.

TABLE VIII. Electron Spin Resonance of Cycloheptatriene Melted Together With Various Compounds and X-Irradiated

Compound	X-ray* (hours)	Spectrum Attributed to Compound**	Spectrum Attributed to Cycloheptatrienyl
acenaphthene	32	weak, ~90 gauss wide, 9 lines with ~9 gauss splittings, saturates easily	none observed
azulene	16	weak, ~50 gauss wide, 13 lines with ~3.5 gauss splitting, difficult to saturate	none observed

*50 kilovolts, 32 milliamps, tungsten target 4 cm from sample.

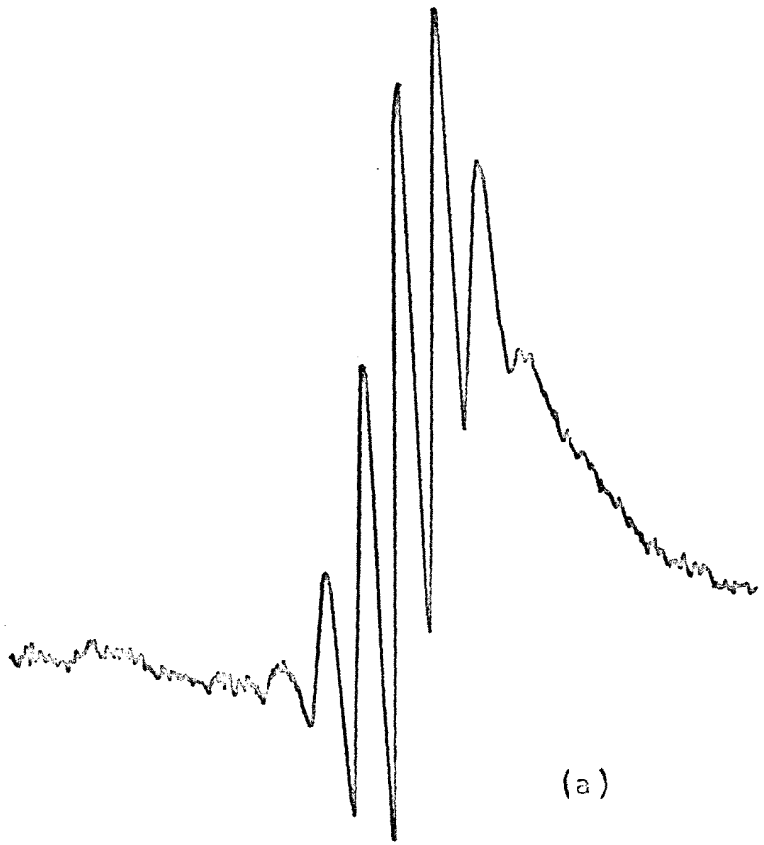
**A blank of x-irradiated compound was taken in each case.

(TABLE VIII. Continued)

Compound	X-ray (hours)	Spectrum Attributed to Compound	Spectrum Attributed to Cycloheptatrienyl
benzoic acid	4 8	moderate, ~90 gauss wide, complicated structure	moderate amount observed
benzophenone	4	moderate, ~15 gauss, saturates easily	large amount observed
biphenyl	15	none observed	none observed
2-bromo-naphthalene	32	very weak, ~90 gauss wide, partially resolved structure	none observed
chloranil	3 16	strong, ~40 gauss wide assymetric	simply melting together gives strong 18 gauss wide line without structure, x-rays effect no further change
1-chloro-naphthalene	8	weak, ~45 gauss wide, no structure	none observed
coronene	16	very strong, ~1500 gauss wide curve with one sharp line at g 2.0036 before x-irradiation, very complex structure appears on the entire curve after x-irradiation	none observed
dibenzo-thiophene	16	weak, ~50 gauss wide, assymetric, little structure, saturates easily	moderate amount observed
1,4-dichloro-benzene	4	very weak, ~25 gauss	none observed
durene	16	weak, ~60 gauss wide 8 lines with ~6 gauss splitting, difficult to saturate	none observed

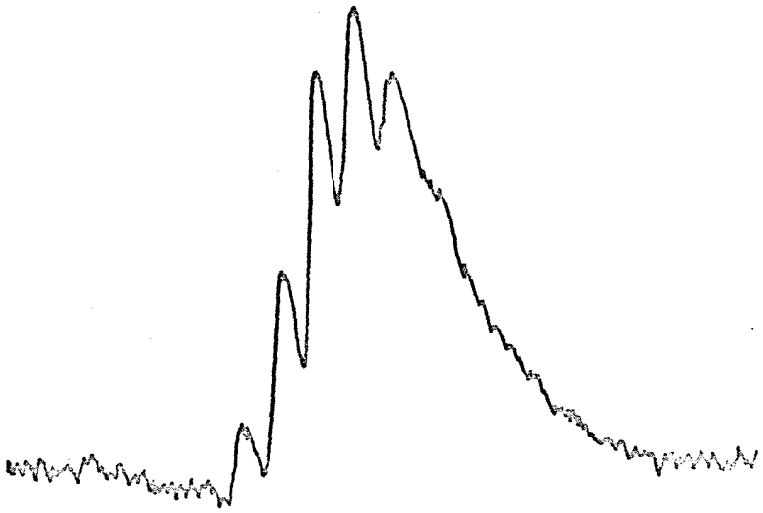
(TABLE VIII. Continued)

Compound	X-ray (hours)	Spectrum Attributed to Compound	Spectrum Attributed to Cycloheptatrienyl
fluorene	18	very weak, ~50 gauss wide, no structure	observed only at high power
fluorenone	18	weak, ~30 gauss wide, 5 lines with ~4 gauss splitting, saturates easily	none observed
hexachloro-benzene	16	weak, ~70 gauss wide, partially resolved structure, assymetric difficult to saturate	none observed
2-methyl naphthalene	15	none observed	no CHT observed but mixed sample had weak, ~70 gauss wide line
2-naphthol	16	weak, ~50 gauss wide, 2 lines almost super-posed	no CHT observed but mixed sample had additional structure
phenanthrene	18	very weak, ~60 gauss wide, partially re-solved structure, saturates easily	observed only at high power
pyrene	32	moderate, ~90 gauss wide, partially re-solved structure, difficult to saturate	none observed
1,3,5-tri-bromobenzene	20	very weak, ~30 gauss wide, no structure, saturates easily	none observed
1,3,5-tri-chlorobenzene	18	very weak, ~30 gauss wide, no structure, saturates easily	none observed
B,B',B"-trichloro-borazole	16	weak, ~130 gauss wide, 7 lines with ~3.5 gauss splitting	moderate amount ob-served
triphenylene	18	very weak, ~40 gauss wide, no structure, saturates easily	moderate amount ob-served



(a)

FIGURE 29. (a) CHT in phenanthrene.



(b)

FIGURE 29. (b) CHT in dibenzothiophene.

G. CYCLOHEPTATRIENYL QUARTET STATE

Longuet-Higgins (21) has calculated that the first excited state of cycloheptatrienyl should be $^4E_1''$. The three unpaired electrons in this state would give rise to a distinctive ESR spectrum. Optical pumping might be expected to populate this state sufficiently for detection by ESR. However (under conditions which would have given a strong ESR spectrum for a naphthalene triplet state in durene matrix) the following systems were tried without success:

(a) CHT-naphthalene at 77° and 4.2°K.

(b) CHT-thiourea at 77° and 4.2° K.

(c) CHT-cycloheptatriene at 77° and 4.2°K.

(d) CHT-argon at 4.2° and 1.5°K.

H. DISCUSSION OF RESULTS AND COMPARISON WITH THEORY

Summary of Experimental Results

The author has studied the CHT radical by ESR in several crystalline environments at temperatures ranging from 1.5° to 300°K. The experimental characteristics peculiar to this radical are the following:

(a) The hyperfine structure undergoes a drastic change at a given temperature, which is different for each crystalline environment.

(b) Above this temperature the spectrum in each of the crystalline environments studied consists of eight equally-spaced lines which are nearly isotropic and have the intensity ratios 1:7:21:35:35:21:7:1. These high-temperature spectra are difficult to saturate (even for CHT in argon at 1.5°K).

(c) Below this temperature the spectra are highly anisotropic and are different for each crystalline environment. These low-temperature spectra are as easily saturated as those of typical free radicals in similar environments.

Table IX contains a summary of the data for CHT in various matrices.

High-Temperature Spectra

The high-temperature spectra of CHT are similar to the spectra of ionic, orbitally-degenerate free radicals in solution (22-25) in that a uniform spin distribution is

TABLE IX. Summary of Cycloheptatrienyl Data in Various Matrices.

Matrix		Transition Temp.	ΔE (cm^{-1})	High-Temperature Form					Low-Temperature Form	
				Temp.	hfs (gauss)	hfsx7	line width	g*** value	extreme hfs(gauss)	g value
Argon (polycryst.)	A	$<1.5^{\circ}K$	<1*	1.5°-4.2°K	3.94	27.6	1.06	2.0037	. . .	. . .
	B	<1.5			3.94	27.6	1.06	2.0046	. . .	. . .
Cycloheptatriene (polycryst.)		10	7**	77	3.97	27.8	2.03	2.0028	28.8	1.9985 +.0015 −.0003
				15	4.00	28.0	2.15	. . .		
Naphthalene	$H_0 \parallel a$	20	14	300	4.08	28.5	1.83	2.0035	30.2 ave. in ac plane	~2.0035 for $H_0 \parallel a$
	$H_0 \parallel b$				3.75	26.3	1.64	2.0037		
	$H_0 \parallel c^*$				3.56	24.9	1.47	2.0038		
	powder				3.75	26.3	2.00	2.0035		
Thiourea Inclusion Compound	$\phi = 0^{\circ}$	40	28	300	3.72	26.1	1.53	2.0033		
				77	3.97	27.8	1.99	. . .		
				45	4.02	28.1	2.70	. . .		
	$\phi = 90^{\circ}$			300	3.82	26.8	1.67	2.0030		
				77	4.05	28.4	2.02	2.0031		
				45	4.01	28.1	2.44	2.0027		
	powder			300	3.77	26.4	1.60	2.0028	35	2.0023

*See footnote p. 43.

**See footnote p. 38.

*** Absolute values should be correct to ±.0004 while relative values should be correct to ±.0001.

observed and the spectra are more difficult to saturate than a number of non-degenerate free radicals in similar environments. A uniform time-average spin distribution is expected when the crystal-field splitting (ΔE) of the orbital degeneracy is small compared to kT (26).

The high-temperature spectra are interpreted as arising from seven equivalent protons, each attached to a carbon atom with spin density 1/7. The fact that the observed single-crystal splittings are nearly isotropic and (27) equal to $1/7|Q|$ [in spite of the high anisotropy of individual (σ-proton)-(π-electron) hyperfine interactions] can be qualitatively shown to result from the facts that (a) there are a rather large number of σ-protons arranged symmetrically around a ring, (b) the C-H fragment hyperfine tensor components A,B,C have the accidental relationships (28) $B \approx \frac{1}{2}(A+C) \approx Q$, and (c) the B Tensor axes are parallel for all protons.

Quantitatively, Silverstone (29) finds that the high-temperature spectrum of CHT in naphthalene is well matched with $Q = -26.8$ gauss, $A = -15.8$ gauss, $B = -26.0$ gauss, $C = -38.6$ gauss, and Gaussian lines of 1.7 gauss width measured from maximum slope to minimum slope. He also finds that molecular rotation or oscillation about the 7-fold axis must be taking place at a frequency greater than 10 Mcs, at least as far down as 77°K.

Theoretical calculation of the CHT-thiourea spectrum is complicated by the six molecules per unit cell and the rapid

tumbling of CHT which probably occurs in this system. The spectrum indicates, however, that the CHT radicals spend most of their time with their normals perpendicular to the tube-axis of the thiourea base-lattice.

The spin-lattice relaxation time (T_1) of the high-temperature spectra does not depend strongly upon the temperature or nature of the lattice; however, T_1 for the low-temperature spectra increases rapidly as the temperature is reduced. There are no large differences in T_1 (low-temperature spectra) for different lattices at the same temperature. The "magnetic pulse" mechanism of McConnell (30) may possibly account for this extraordinarily constant spin-lattice relaxation time in the high-temperature orbitally-degenerate form of CHT. At room temperature, T_1 must be at least 2×10^{-7} sec (according to measured line widths). The line widths of CHT (high-temperature form) in argon are one-half those of CHT in proton-containing matrices. Therefore, in the argon matrix, T_1 must be at least 4×10^{-7} sec. A simple computation shows that the broadening expected from nearby protons in the lattice is of the order of a few gauss. This indicates that intermolecular (nuclear-dipole)-(electron-dipole) interactions are the main source of line broadening for CHT (high-temperature form) in proton-containing matrices at lower temperatures. The "spin switching" mechanism proposed by McConnell (26) is probably responsible for the broadening of and the decrease in intensity of the high-temperature spectra just above the transition temperature.

When $kT = \Delta E$ the number of CHT radicals in the lower state is 2.8 times the number in the higher state; this should give a quite noticeable change in the ESR spectrum because the high-temperature spectrum would lose approximately 2/3 of its intensity. Therefore, it is assumed that at the measured transition temperature, $\Delta E \approx kT$. By this criterion, the Jahn-Teller distortion energy (4) of the CHT ring must be less* than 1 cm^{-1}. Further, the spin-orbit interaction must also be less than 1 cm^{-1}. If the orbital angular momentum (not measured so far) were large enough, it would be possible to remove the orbital degeneracy with a magnetic field attainable in the laboratory.

Low-Temperature Spectra

Silverstone (29) finds that both the LCAO-MO-SCF and the Pariser-Parr methods give rough agreement with the experimental spectrum of CHT in naphthalene (low-temperature form). He has matched the experimental and theoretical spectra for one orientation of CHT-thiourea (low-temperature form).

Conclusions

CHT is a planar regular heptagon with an orbitally degenerate ground state. This degeneracy can be removed with a crystalline electric field. The wave functions, after the degeneracy has been removed, are determined by the crystal field. The Jahn-Teller distortion of the ring and

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*See footnote, p. 43.

the spin-orbit interaction in this degenerate molecule must be less than 1 cm^{-1}. Therefore, the Born-Oppenheimer approximation does not hold. The LCAO-MO-SCF and the Pariser-Parr methods give approximate agreement with experiment for this cyclic, non-alternant hydrocarbon free radical.

PART II

AUXILIARY APPARATUS

A. LOW-TEMPERATURE ELECTRON SPIN RESONANCE SYSTEM

Field-Dependent Noise

The dewar used in this low-temperature ESR system was originally designed by O. H. Griffith (31) for ESR studies of optically excited triplet states in organic crystals. This dewar has been called "Big Bertha" in these laboratories (BB for short).

BB had a very high noise level in "her" original configuration. This particular type of noise became known variously as "field-dependent noise" and as "golden garbage". This field-dependent noise came about if, and only if, microwave power, 100 Kcs modulation field, low temperature* (for example, 77°K), and steady magnetic field were all present simultaneously. There seemed to be a small threshold value for the steady magnetic field after which the noise increased steadily with increased field strength. An increase in microwave power and/or 100 Kcs modulation field caused a rapid increase in the noise. The random fluctuations of the chart recorder pen were of the same order or magnitude as the deflection from a "moderate" ESR signal**. This was highly unsatisfactory for the experiments described in Part I of this thesis because the CHT ESR signals were never much stronger than "moderate".

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*Donald Halford has recently observed field-dependent noise at room-temperature in other cavities.

**The Varian V-4500 ESR Spectrometer with V-4500-41A Low-High Power Microwave Bridge and V-4560 100 Kcs Field Modulation and Control Unit was used for these experiments.

If the microwave cavity were to vibrate randomly with time at 100 Kcs in such a manner as to modulate the microwaves, noise in proportion to the microwave modulation would be amplified and displayed on the recorder. This type of noise would be expected to increase with microwave power and with mechanical vibration amplitude. Also, the latter would increase with 100 Kcs modulation amplitude and with static magnetic field if the vibration were driven by the interactions of the static magnetic field with (a) the 100 Kcs modulation coils or (b) the eddy-currents caused by the 100 Kcs signal.

One good method to transform vibration into microwave modulation is via the tuning screw, which controls the microwave power reflected from the cavity. Another mechanism would be the relative movement of two parts of the cavity between which microwave current flows, such as between the body and end plates of rectangular cavities operating in the TE_{01} modes*. Differing or non-uniform coefficients of expansion could cause parts of the cavity to become loose or warped because of changes in temperature.

A. F. Hildebrandt suggested that, if the microwaves were being modulated by a 100 Kcs mechanical vibration of the cavity, then it was likely that a different modulation frequency would have a much different effect on the vibration and hence on the microwave modulation. Indeed, simultaneous

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*The original cavity used in BB was a rectangular TE_{011}.

modulation at 100 Kcs and 400 cps completely eliminated the field-dependent noise.

The author found that the following steps would eliminate the field-dependent noise for single-modulation (100 Kcs) experiments:

(a) Make all mating surfaces as flat and smooth as possible using emery paper.

(b) Carefully avoid direct contact between modulation coils and cavity.

(c) Securely tighten all screws, but do not tighten them enough to warp the parts.

The ESR system was still not entirely satisfactory, however, because the poor Q ($\sim$1000) did not allow resolution of the CHT in naphthalene low-temperature spectrum. Therefore, a new cavity was designed.

Microwave Cavity

The new microwave cavity was designed to operate in the cylindrical TE_{011} mode for the following reasons:

(a) A high Q ($\sim$10,000) is both theoretically and practically attainable.

(b) Samples can be rotated with very little cavity frequency change.

(c) Current-carrying joints would be at a minimum, thus reducing the probability of field-dependent noise.

The nominal design frequency was 9600 Mcs.

Aluminum and paper-base Bakelite were chosen as materials because of their almost equal expansion coefficients and because of the good thermal and electrical conductivity of aluminum.

Figure 30 shows a cross-section of the cavity assembly. The aluminum part designated A (shown in detail in Fig. 31) serves (a) as the end plates for the cavity, (b) as a coupling plate for the cavity, (c) to hold the crystal mount, and (d) to hold the cylindrical part of the cavity (B). Light or x-rays may be shined upon the sample through interchangeable quartz or beryllium windows, respectively. The windows can be replaced with a quartz tube which can be slipped into or out of the cavity at will. Aqueous peroxylamine disulfonate ion or polycrystalline diphenyl picryl hydrazyl inside the quartz tube is then used as an internal standard. Alternately, the windows in parts A and C may be plugged in order to insure that room temperature radiation does not warm the sample directly.

Part B, made of bakelite (Fig. 32), is silvered according to the method of Chester et al (32), except that only the acid cleaning-bath is used. This part must be carefully emery-papered after silvering so that it will fit snugly into part A. It should be stressed that the angles must be square and the surfaces flat for parts A and B, or else field-dependent noise may result.

Part D (Fig. 33) is the crystal mount. It is made of aluminum and is hard anodized on the surface which mates with

part A, in order to prevent galling. To insure good heat transfer between these two parts, they are carefully lapped in with Lava (brand) soap. Other standard abrasives were found to imbed in the soft aluminum. That portion of D which protrudes into the microwave cavity should be silver plated, because paramagnetic impurities in the surface layer of aluminum oxide will give an ESR signal, especially at low temperatures. Part D is held firmly, but not so tightly as to bind, to part A by a phosphor-bronze clip-ring. The crystal to be studied is attached to the crystal mount with Kwiram Glue*.

The crystal mount can be rotated during the course of an experiment (even at 4.2°K) by a hexagonal cross-section nylon rod. This rod is glued into a 0.25" stainless steel rod which passes into the vacuum through a neoprene o-ring. The o-ring is coated with high-vacuum grease and is held against the stainless steel rod with a compression nut. A large wheel marked off in degrees and attached to the outer end of the 0.25" rod and a stationary pointer attached to the outside of the dewar are used to rotate the crystal a known amount. Figure 30 illustrates the construction of this crystal-rotation device. At room temperature the crystal-rotation device and the crystal mount are misaligned by .070", but when liquid helium or liquid nitrogen are in the dewar, they are very nearly in line. However, the

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*See page 8 of this thesis.

device can be tilted to engage the slot in the crystal mount at any temperature. (A helium-sensitive leak detector found no vacuum leak, even when the crystal-rotation device was worked vigorously.) A similar device is used to rotate the turning screw (Fig. 34).

Modulation Coils

The modulation coils were designed to be operated by a Varian V-4560 100 Kcs Field Modulation and Control Unit. Each coil consists of approximately 40 turns of #34 Bondeze* insulated copper wire wound on a 40 mm diameter form. The cross-section of the coils is approximately 2.5 mm square. The coils are attached with Kwiram Glue to the outside of a bakelite tube (1 mm wall) which has been fitted tightly into the aluminum heat shield of the dewar (Fig. 35). The comparatively large distance of the modulation coils from the cavity reduces the probability of field-dependent noise. The coils are impedance-matched to the Varian modulation unit by a variable capacitance (1000-1365 $\mu\mu$f) in parallel with the coils. Maximum 100 Kcs modulation amplitudes of 13 gauss are attained. Electrical connection to the modulation coils is made through a plug (shown at the bottom of Fig. 30). The aluminum heat shield of the dewar is slotted at the bottom in such a manner that only small area closed electrical paths about the modulation field between the coils are possible (Fig. 35), and hence little eddy currents can be generated there.

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*Trade name of Phelps Dodge Copper Products Corp.

Temperature Control

BB can be kept to within a degree or two of any desired temperature between 1.5° and 300°K. A regulated flow of nitrogen gas through a heat exchanger cooled with liquid nitrogen and thence into BB is useful for temperatures between 77° and 300°K. Cold helium gas is used between 4.2° and 77°K. Liquid helium is used between 1.5° and 4.2°K. The temperature is constantly monitored at will with a copper-constantan thermocouple which is imbedded in the microwave cavity.

In order to obtain cold helium gas with which to cool BB, the following method was used successfully: the liquid helium transfer tube was placed with one end well into BB and the other end below the liquid helium level in the storage dewar; the storage dewar was then pressurized to a few inches of water pressure with dry helium gas. A Moore Nullmatic (0-50 inches water) pressure regulator was used satisfactorily. Liquid helium forced up into the transfer tube will vaporize and pass through the tube into BB. The warmed helium gas which escapes from the top of BB is monitored with a Matheson type 604 flowmeter. The flow rate, and hence the temperature, is easily adjusted by either increasing or decreasing the pressure in the storage dewar. Thus if 0.7 liters of liquid helium are made to boil off per hour, then BB can be cooled from 77°K to 4.2°K within one hour.

ASSEMBLY, DEWAR, ESR, LOW TEMPERATURE

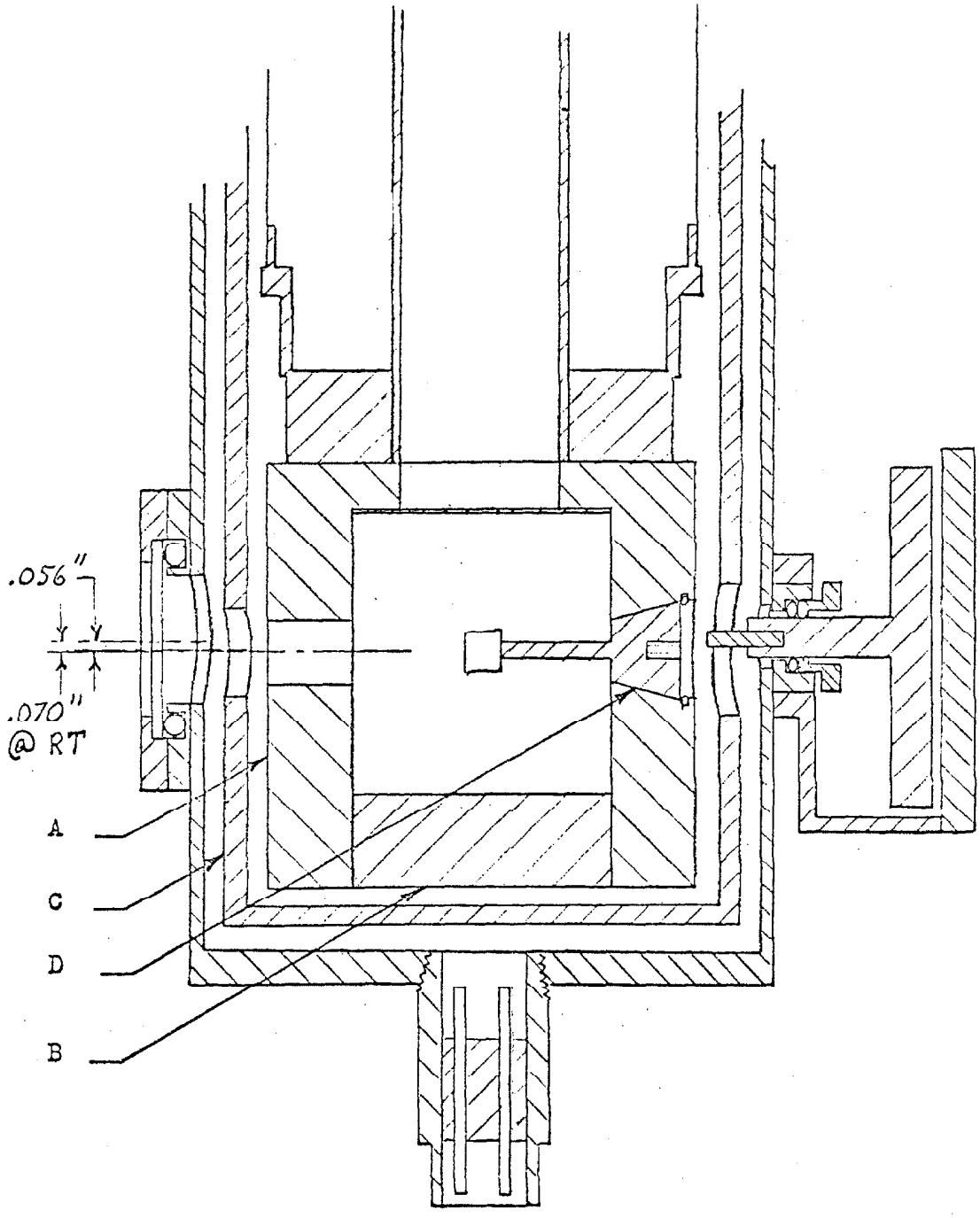
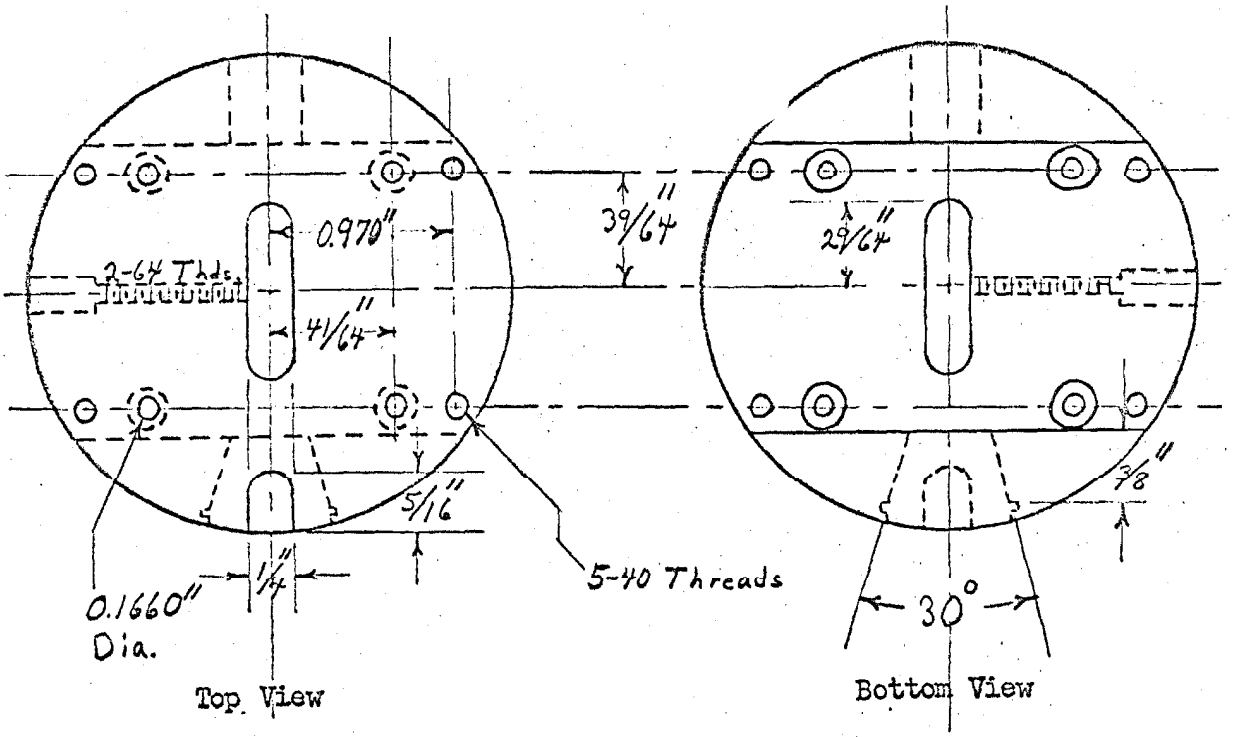


FIGURE 30. ESR dewar assembly.

CAVITY, ESR, LOW TEMPERATURE #A



Material: Aluminum

Finish: Fine Machine and Flat

Silver Plated .0005"

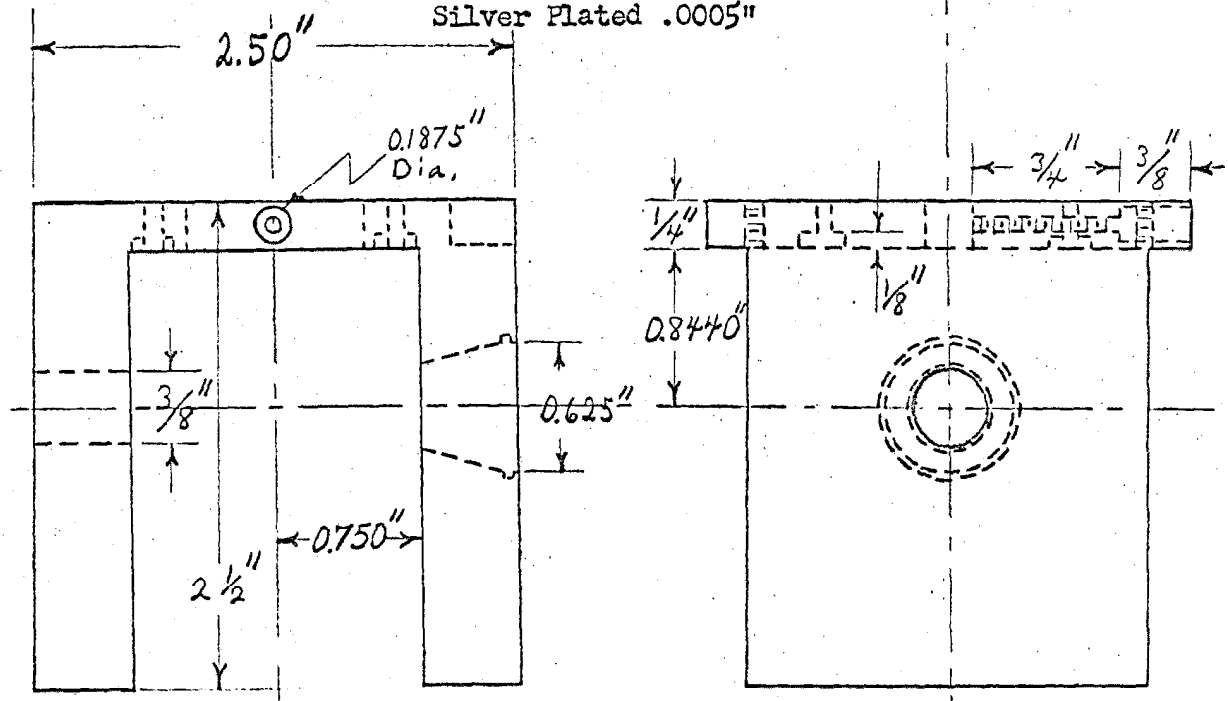
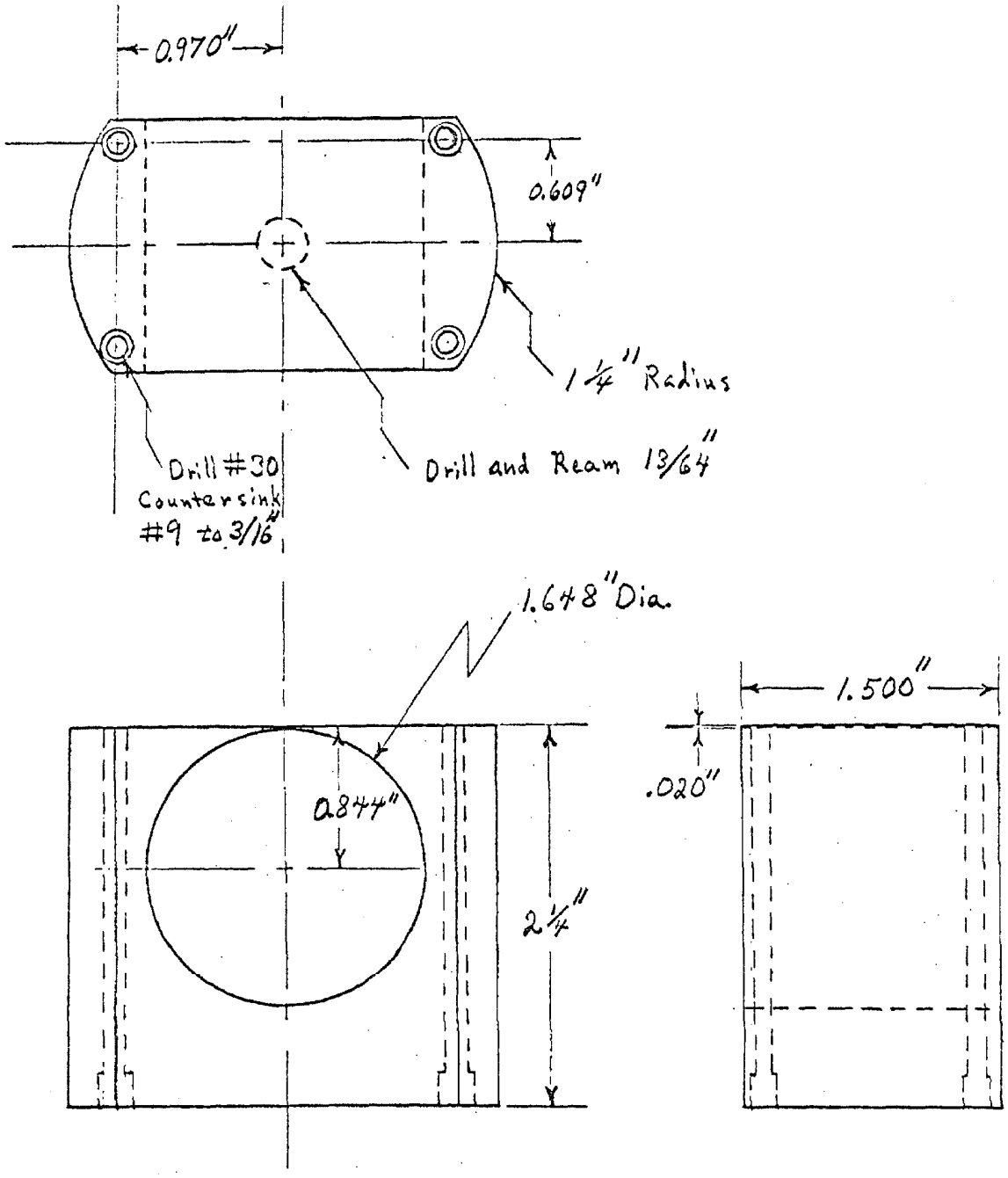


FIGURE 31. Part A.

CYLINDER, CAVITY, ESR, LOW TEMPERATURE #B

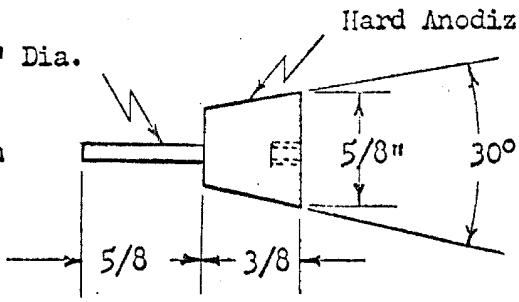


Material: Paper Base Bakelite. Finish: Fine Machine and Flat.

Chemically Silver at least 0.001"

FIGURE 32. Part B.

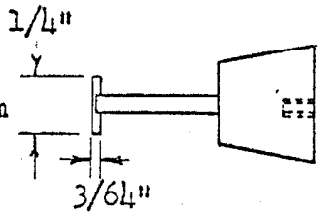
MOUNT, CRYSTAL, CAVITY, ESR, LOW TEMPERATURE #D



Material: Aluminum

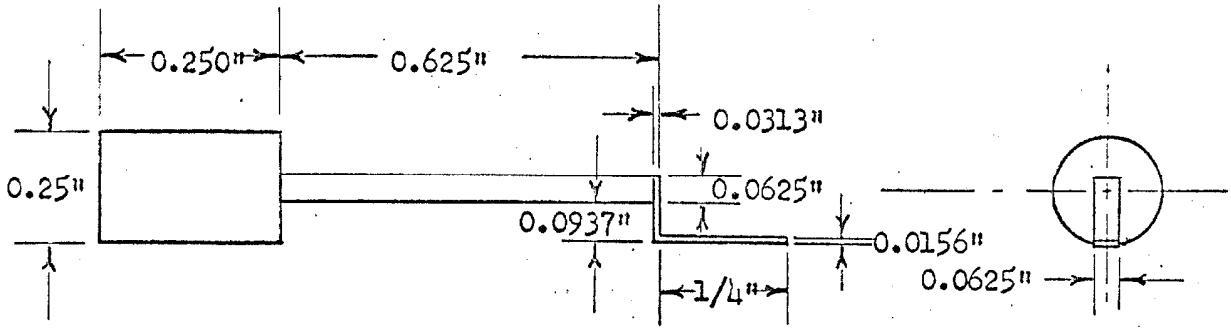
Cut 1/8" Hex in Head

Crystal Mount for Naphthalene ab Plane.



Material: Aluminum and Brass

Crystal Mount for Thiourea Made from Naphthalene ab Plane Mount by Inserting 1/64" Sheet Brass into Milled Slot.



Material: Cu

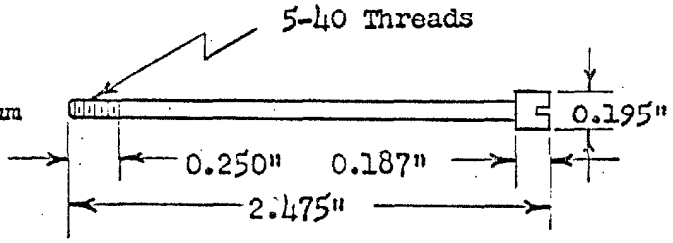
Side View

End View

Crystal Mount for Naphthalene ac Plane. To be Slip Fit in Anodized Taper.

FIGURE 33. Part D.

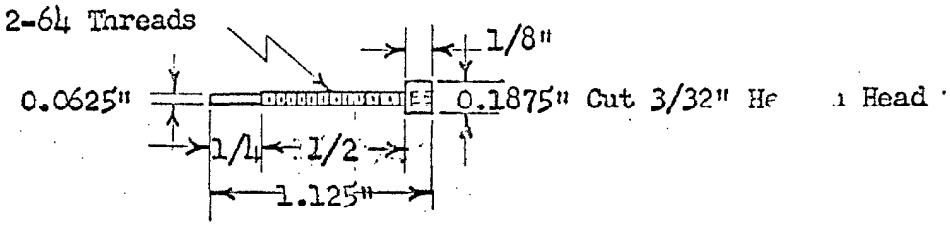
SCREWS, CAVITY, ESR, LOW TEMPERATURE #E



Material: Aluminum

Cylinder Holding Screw

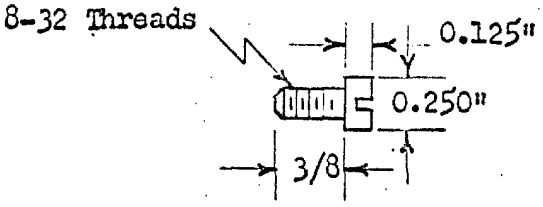
Four (4)



Material: Brass Cut 3/32" He ı Head

Tuning Screw

One (1)



Material: Brass

Coupling Plate Screw

Four (4)

FIGURE 34. Part E.

CORE, SEAL, HEAT, DEWAR, RESONANCE #C

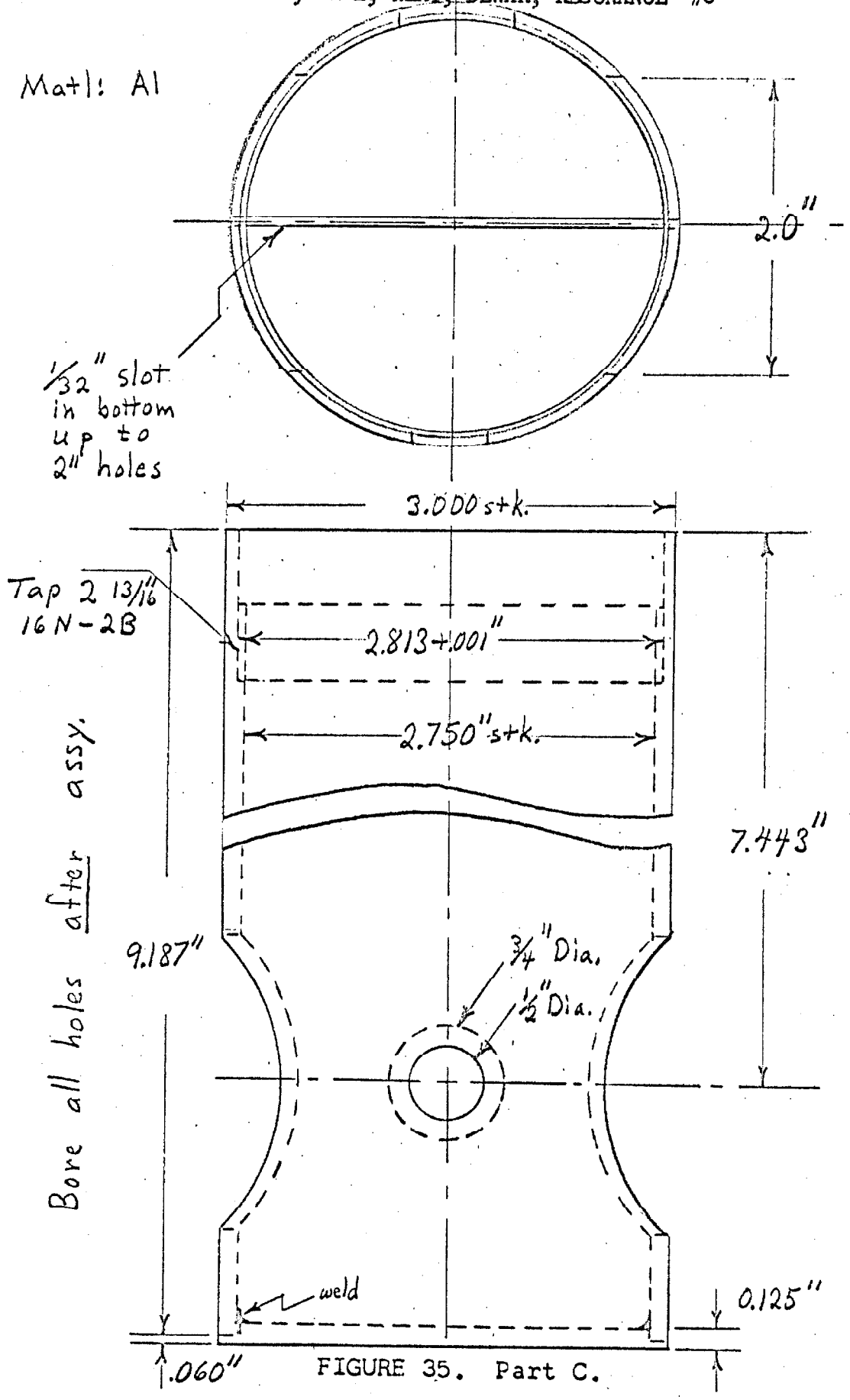


FIGURE 35. Part C.

B. ZONE REFINERS

The ever-increasing use of organic single crystals and the purity requirements for these crystals in the research of the McConnell group led quite naturally to the use of zone refining. This technique not only removes impurities very similar to the major component, but also those substances which produce inferior crystals when occluded.

Zone refining, which was invented by W. G. Pfann (33,34) in 1952, is in essence an automated method for doing fractional crystallization from the melt with many recombinations of the fractions. The procedure consists of repeatedly moving a molten zone through a long thin charge, which results in concentration of impurities in both ends of the sample. The requirements for the separation of two substances by zone refining are the same as those for separating the two substances by fractional crystallization from the melt, i.e., that they do not decompose upon melting, that they are not in eutectic concentrations nor between two eutectic concentrations, and that the liquidus and solidus are not the same curve. These requirements are met by many of the common reagent-grade organic chemicals.

The way to pass the largest number of molten zones through a sample in the shortest time is to separate many molten zones by as short a frozen zone as possible. In the author's apparatus the molten zones are maintained by coils of resistance wire, and the frozen zones are kept cool by tap water running through coils of copper tubing. The molten

zones are moved through the sample by a clock motor and pulley. See Figure 36.

For the solids such as naphthalene, pyrene, indole, and coumarin the sample tube is held at 45° to the horizontal as a workable compromise between removal of dirt and quality of the freezing interface. The convective mixing in the molten zone is best for a vertical interface; however, the dirt present in the usual "reagent grade" samples falls to the end of the tube more readily if it is inclined. For tubes containing material without dirt the tubes may be used horizontally; however, it then becomes necessary to install a moveable teflon partition to maintain the airspace in the tube (the airspace is necessary to prevent an explosion).

The glass sample tube is filled with either molten or powdered material and is usually degassed by at least three freeze-thaw cycles under a strong vacuum and sealed off under a sufficient nitrogen pressure to prevent sublimation. The degassing is necessary to prevent explosions with some substances, notably naphthalene. The tube is usually passed through 15 to 20 zones, at which time the impurities should be very near their ultimate distribution (for example, for small concentrations of indole in naphthalene this would be 10^{-4} times the original concentration of indole, at the purer end of the charge). The purer half of each of two samples can be combined into one tube and re-refined to great advantage.

Zone refiners of the design shown in Figure 36 have been built for 8, 10, 13, and 20 mm tubes, and it would not be difficult to build zone refiners either larger or smaller than these. Chemicals with melting points of from 49°C (benzophenone) to 199°C (triphenylene) have been purified in these refiners, and the temperature range could easily be lowered by circulating a refrigerant through the cooling coils or raised by insulating the apparatus to keep down convective heat loss to the air.

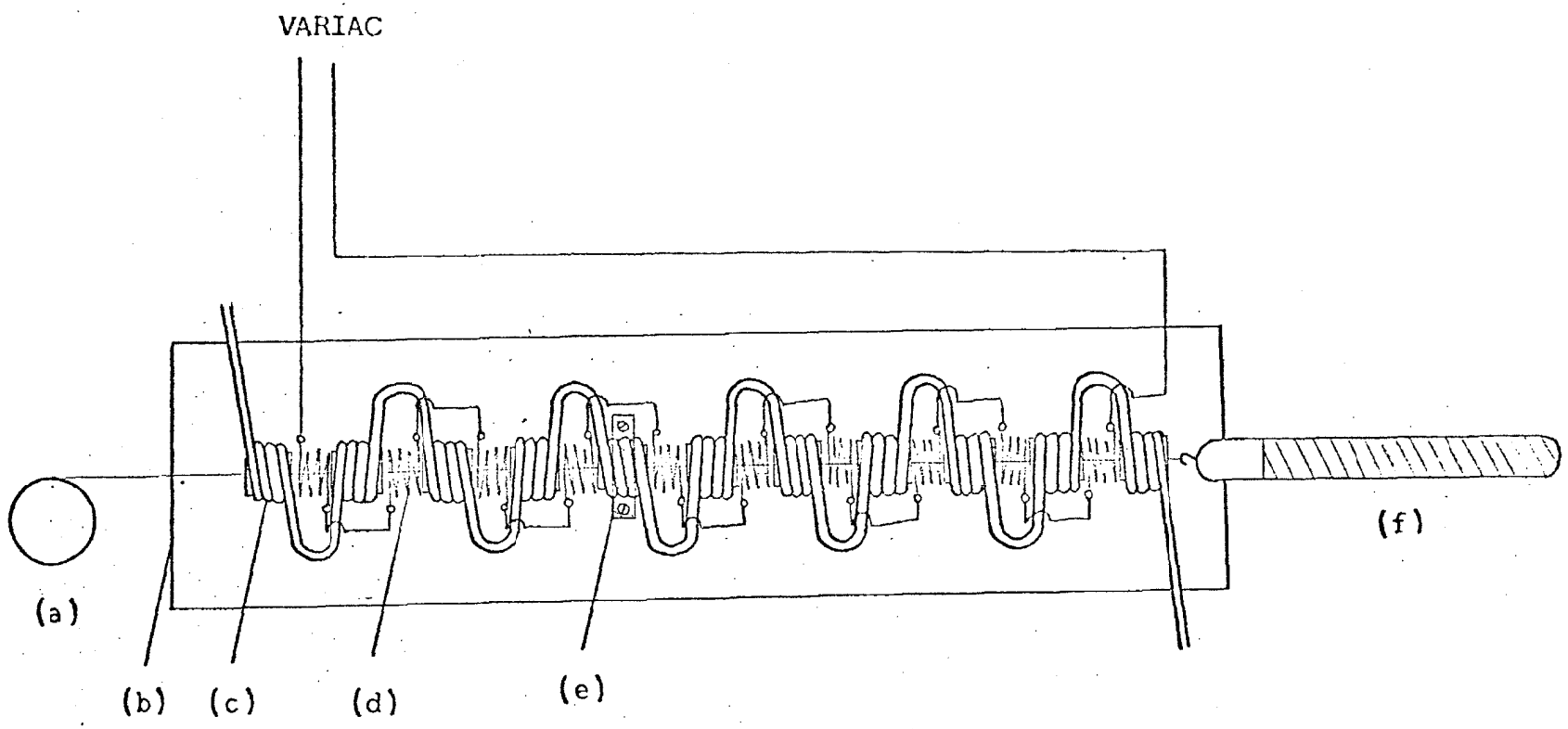


FIGURE 36. Zone Refiner. (a) 3 to 6 rpd motor with 1 to 3 inch pulley; (b) mounting board; (c) copper tube cooling coil with brass insert; (d) resistance-wire heating coil; (e) brass strap for securing cooling coils; (f) sample tube containing material to be zone refined.

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PROPOSITION 1

A design for a low-temperature ESR system is proposed. It has the following features:

(a) Single crystal ESR spectra can be observed as H_o is rotated in a given plane.

(b) Powder (contained in a suitable holder) ESR spectra can be observed.

(c) ESR of free radicals deposited from the vapor phase can be observed.

(d) The samples can be bombarded with ultraviolet light, x-rays, or electrons during the course of an experiment.

(e) The sample is kept at a known, uniform temperature which can be varied from 1.5^{o} to $300^{o}K$ at will.

(f) The Q is very high (conservatively predicted to be 10,000).

(g) Field-dependent noise should be no problem (for 100 Kcs modulation scheme).

(h) There will be no noise from refrigerants boiling in the cavity (the cavity is entirely evacuated).

(i) Only a small quantity of liquid refrigerant is needed in order to use this system.

The first part of this discussion concerns the use of this ESR system <u>with superheterodyne detection.</u> The cavity is designed to be used with the McConnell group standard

ESR dewar with the modifications to the helium container which are apparent in Figure 1. The low-temperature ESR system is shown assembled in Figure 1. The coupling plate (Fig. 2) and the cylinder (Fig. 3) are fabricated from brass. They are then burnished, electrolytically silver plated to .001", and burnished again. Care must be taken to insure that mating surfaces are flat and parallel. The helium and nitrogen heat-shields (Fig. 1) are made either of electrolytic copper or free-cutting, leaded copper. They are then chrome plated and polished. The helium heat-shield can be rotated by a .250" nylon rod (Fig. 1) in order to either expose or cover the windows in the cavity. A neoprene o-ring and compression nut prevents leakage around the nylon rod. The tuning screw and the cylinder-holding screws are made of brass (Fig. 4).

The windows can be either quartz or beryllium for use with light or x-ray bombardment respectively. Alternately, an electron gun can be installed in one of the windows for electron bombardment of the sample. For gas deposition experiments, a capillary is inserted into the cavity through one of the windows.

For 100 Kcs field-modulation experiments, the coupling plate is made of 1100 aluminum alloy. It is then burnished and electrolytically silver plated to .001". The cylinder is made of paper-base bakelite. It is then chemically silver plated (1) and burnished. The helium heat-shield is fabricated of sintered aluminum oxide. The nitrogen

heat shield has two 2" holes for mounting the 100 Kcs field-modulation coils. These holes must, of course, be connected by a slot to reduce eddy currents. A spur gear on the nylon rod is used to rotate the nitrogen shield and hence the modulation coils for the 100 Kcs field-modulation experiments (not shown in figures).

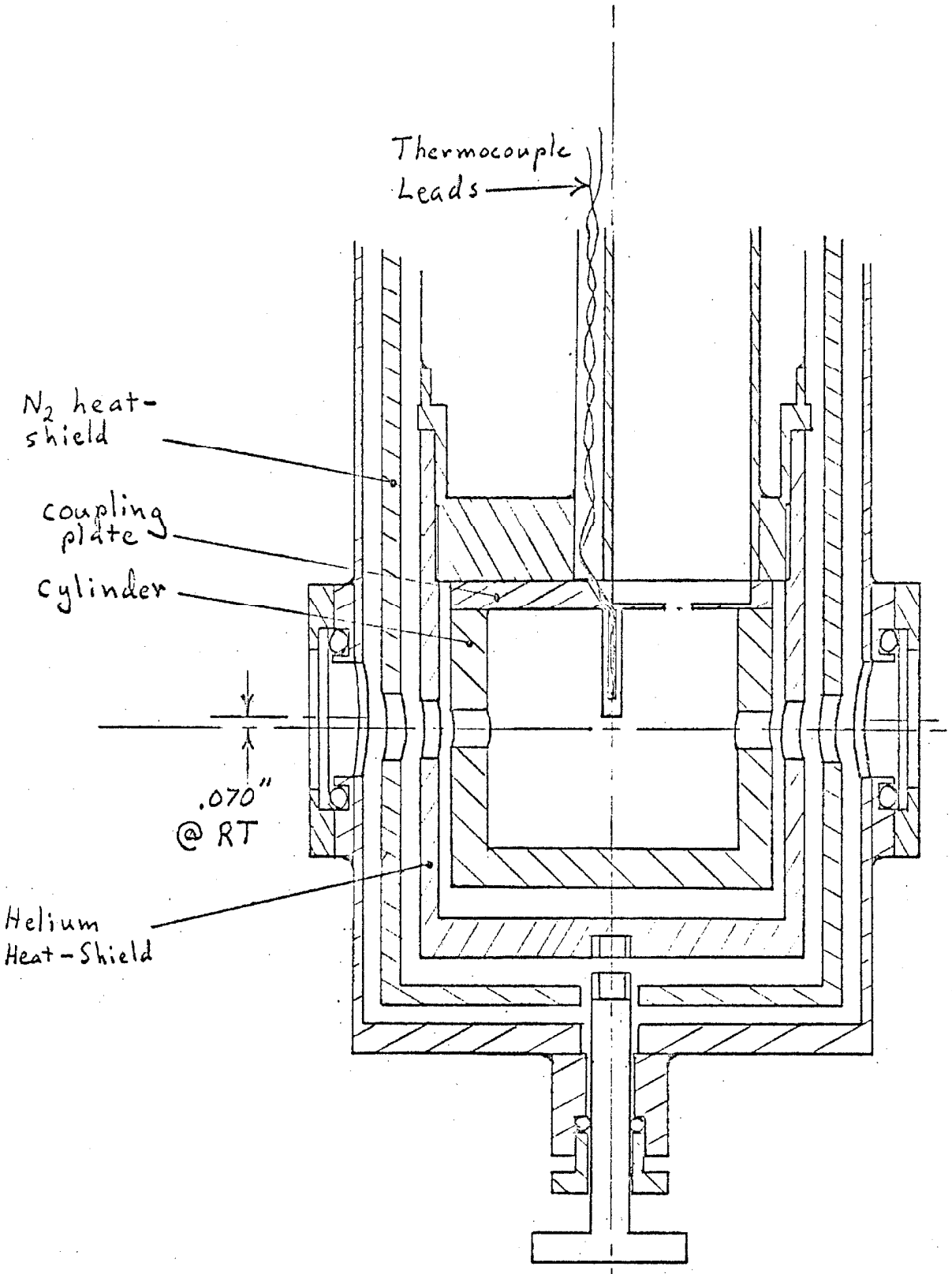


Figure 1. Dewar Assembly.

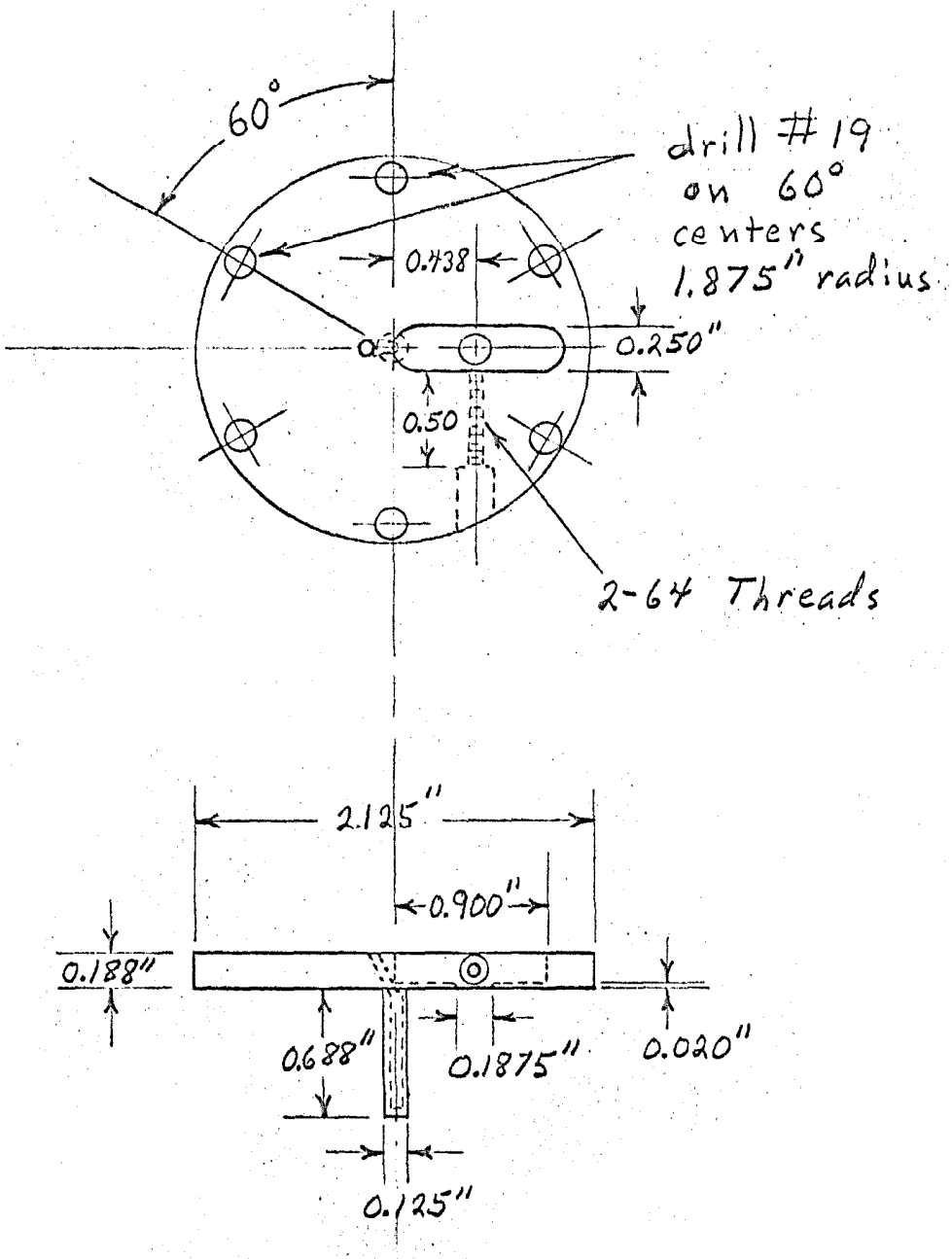


Figure 2. Coupling Plate.

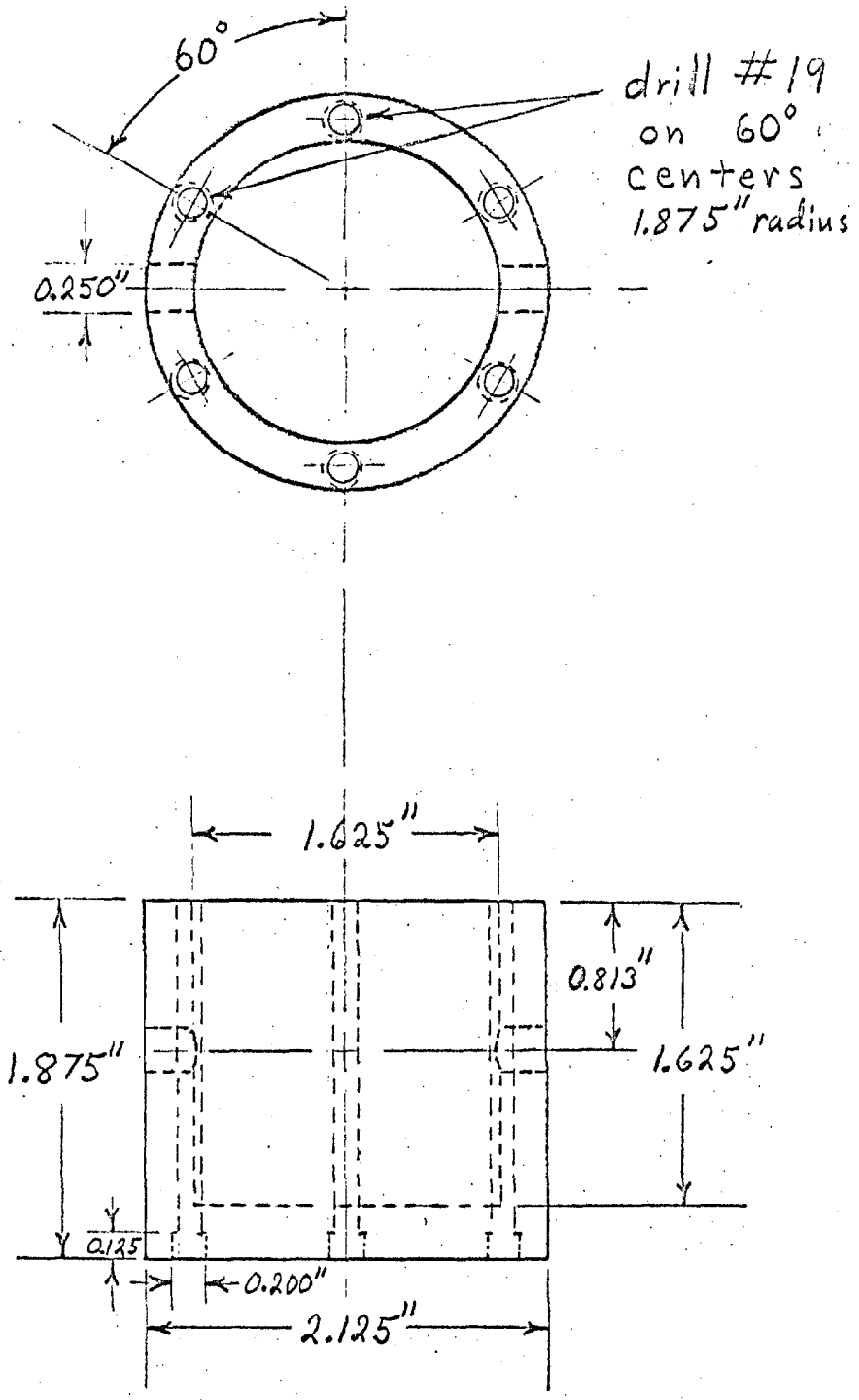
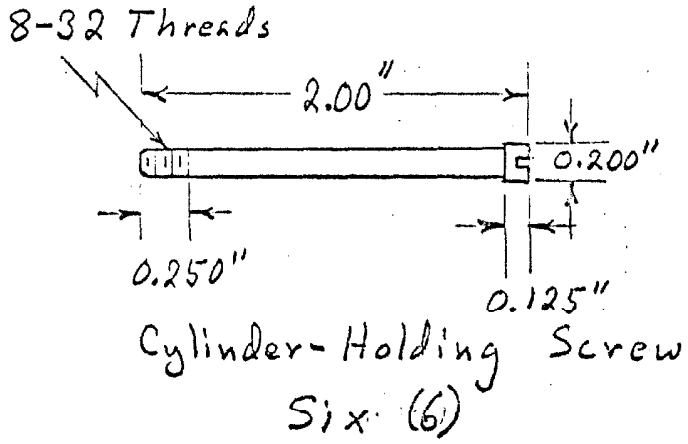


Figure 3. Cylinder.



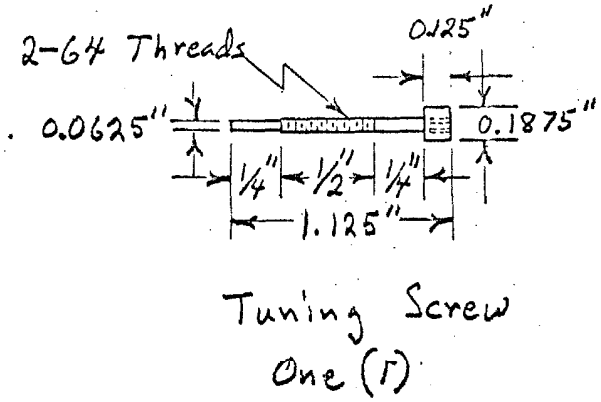


Figure 4. Screws.

PROPOSITION 2

Cyclopropenyl radical (C_3H_3) has been studied theoretically (2,3), but it has not yet been experimentally observed. An experiment designed to produce C_3H_3 for study by ESR is proposed.

Relatively pure cyclopropene can be easily prepared by the method of Wiberg (4). Cyclopropene vapor under low pressure (.1 mm Hg or less) is passed through a 1 x 100 mm quartz capillary. A very intense ultraviolet source* is carefully focused on the tip of this capillary. The cyclopropene vapor will be photolyzed, and one of the principal products will probably be the cyclopropenyl radical. The radicals thus formed travel through high vacuum for about 3 cm before condensing on a cold finger. Rare gases or other appropriate inert diluents may be added to the free radical stream just before deposition. It is probably impossible to make a large concentration of radicals in the presence of the inert diluents**because of collisional deactivation of the excited cyclopropene; this is the reason for diluent addition after photolysis. It is noted that confining the cyclopropene vapor to a 1 mm capillary during the irradiation allows very high ultraviolet light intensities to be used for the photolysis.

ESR of the deposit should give a spectrum with four equally spaced lines of intensity ratios 1:3:3:1 if C_3H_3 has

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*For example, an Osram HBO 100 W1.

**The ratio of diluent to cyclopropene should be approximately 100:1.

been formed. The study of the effect of ring strain on the hyperfine tensor and on the spin orbit coupling in this radical could prove interesting. If the C_3H_3 radicals were cooled to a low enough temperature that a nonuniform spin distribution resulted, it might be practically possible to analyze the spectrum in terms of current theory (although the sample would be polycrystalline, each molecule would give only eight absorption lines).

PROPOSITION 3

The pi-electron spin-orbit interaction, Λ, in aromatic molecules has been calculated to be very small (5,6) compared to that of atomic carbon (~ 28 cm^{-1})(5). McClure (5) has inferred from experimental evidence on phosphorescent lifetimes that Λ is of the order of magnitude of a cm^{-1}. The results of this thesis indicate that Λ is not greater than a few cm^{-1}. McConnell (7) has recently suggested that a spin-orbit interaction of $\sim .5$ cm^{-1} or greater can account for the following observations in ESR spectra of orbitally degenerate states of aromatic ions:
(a) the short (compared to non-degenerate aromatic ions in similar environments) spin-lattice relaxation time noticed by Townsend and Weissman (8) in triphenylene negative ion and by Bolton and Carrington (9) in coronene positive ion;
(b) the unusually broad hyperfine lines observed (8-11).
No other mechanism has yet been postulated which accounts for both of these observations. The pi-electron spin-orbit interaction, if known, would shed light on the suggestion of McConnell (7). Furthermore, it would be of great use in calculations of radiative and non-radiative transition probabilities in aromatic molecules.

For an orbitally degenerate free radical there are three special cases possible for the spin-orbit interaction:
(a) the degeneracy is removed by the spin-orbit interaction;
(b) the degeneracy is removed by the crystal electric field;
(c) the degeneracy is removed by a strong magnetic field.

For case (a)

$$g_{\parallel} = 2(1 \pm m_{\ell})$$

$$g_{\perp} = 0.$$

Where $g_{\parallel}$ and $g_{\perp}$ are the spectroscopic splitting factors for H_o parallel and perpendicular, respectively, to the symmetry axis of the electron orbit, and m_{ℓ} is the orbital angular momentum. For case (b)

$$g_{\parallel} = 2(1-m_{\ell}\Lambda/\Delta E)$$

$$g_{\perp} = 2.00.$$

Where ΔE is the crystal-field splitting of the (degenerate) orbital states. For case (c) the Paschen-Back effect will be observed and the orbital angular momentum will be coupled directly to the strong magnetic field.

If the g value for either case (a) or (c) can be obtained and if the g value for case (b) can be studied as a function of the crystal field-splitting, then m_{ℓ} and Λ can be determined. Case (a) might possibly be obtained by the ESR of cycloheptatrienyl in a solid rare gas matrix at very low temperatures. Very high field (10,000 to 100,000 gauss) ESR would be used to obtain case (c). The study of g value variation as a function of ΔE could be done by subjecting the sample to very high hydrostatic pressures. There are, of course, experimental difficulties to taking ESR spectra at low temperatures and high pressures simultaneously. However, 400 atmospheres is available from super-high pressure gas cylinders, and low-temperature ESR can probably be done at these pressures. Another, more easily performed, method

for varying Δ E would be to use a series of cycloheptatrienyl in solid rare gas matrices. This experiment could be done in an apparatus similar to that described in Proposition 1. However, the symmetry changes of the matrix (with respect to the cycloheptatrienyl) might partially mask the results.

PROPOSITION 4

The second and third triplet states of benzene have not yet been observed experimentally. A direct optical absorption experiment is troubled by the difficulty that the very small amounts of impurities present have stronger absorptions than that expected for benzene triplet. However, magnetic rotation spectroscopy "sees" only transitions between two states at least one of which is changed in energy or split by a magnetic field. Therefore, the strong singlet-singlet absorptions of the impurities would not mask the benzene singlet-triplet transition as it would in an absorption experiment.

The spectrum of the light transmitted through crossed polarizing prisms when a magnetic substance is placed between the prisms so that the light passes along the magnetizing field is the magnetic rotation spectrum (12) of the substance. Sharp lines (of the order of the Zeeman splitting) are required in order to observe magnetic rotation spectroscopy. The magnetic rotation spectra of formaldehyde, glyoxal, acrolein, and benzoquinone corresponding to the singlet-triplet transitions have been observed in the vapor (13,14). Benzene single crystals at 20°K have 2-4 cm^{-1} wide absorption bands (15) for the singlet-singlet absorptions and the singlet-triplet absorption bands should be at least as narrow. This requires a magnetic field for the experiment of at least 10,000-12,000 gauss which is easily obtained.

For a weak transition the rotation expected (12) is

$$\phi = \frac{4\ fNe^2}{5\ mc\alpha}\ .$$

Where f is the oscillator strength of the transition, N is the number of molecules per cc, α is the splitting of the magnetic sublevels in frequency units, m is the electron mass, and c is the speed of light. For pure benzene, if $f = 10^{-11}$ and $\alpha = 1\ cm^{-1}$, then

$$\phi = 1.7 \times 10^{-2}\ \text{radians/cm.}$$

If the factor of 20 enhancement obtainable by multiple reflection between thin metallic films (16) is added, then

$$\phi = .34\ \text{radians/cm.}$$

Therefore, if a one cm thick single crystal of benzene at $1.5^{\circ}K$ were used it might be possible to observe a rotation of 20° for plane polarized light at the wavelength corresponding to the singlet-triplet transition in benzene.

PROPOSITION 5

At low temperatures, solid free radicals ($S = \frac{1}{2}$) exhibit an orderly pairing of spins to form dimers with a singlet ground state and a low lying triplet state (17,18). This triplet state becomes thermally populated as the temperature is raised. The ESR spectrum consists of two sharp lines with a separation dependent on the zero field splittings of the triplet state (19). These triplet states are called triplet excitons because they are delocalized or move about the crystal (20). The solid free radicals used for these studies have small singlet-triplet splittings; for example, in Wurster's blue perchlorate the splitting is calculated to be ~ 246 cm^{-1} (21). Low temperatures are therefore required in order to study the triplet excitons at low concentrations. Besides this, large single crystals free of paramagnetic impurities are very difficult to obtain (21).

It should be useful, from a theoretical point of view, to study exciton systems with a large singlet-triplet splitting. Such a system might be naphthalene single crystal; however, the ESR of this system has not yet been observed. On the other hand, breaking a classical chemical bond would also give a large singlet-triplet splitting. Bitropyl-thiourea inclusion compound is probably, therefore, a system which will exhibit triplet exciton behavior. The central bond dissociation energy of bitropyl, C_7H_7-C_7H_7, is estimated (22) to be 35 kcal/mole $= 12{,}000$ cm^{-1}. Each

bitropyl molecule can be thought of as having an excited triplet state, consisting of two tropyl radicals, 12,000 cm^{-1} above the singlet ground state. The thiourea base-lattice consists of hollow hexagonal tubes of infinite length (23). The included molecules, bitropyl in this case, fit into these tubes in a regular manner, but there are no chemical bonds formed between the lattice and the included molecules (23). The attempt by the author to make the bitropyl-thiourea inclusion compound was very successful. Evaporation of a methanol solution containing six parts thiourea to one part bitropyl yielded good-sized hexagonal needles of the inclusion compound. Room temperature x-irradiation of these crystals gave a good yield of cycloheptatrienyl radicals as measured by ESR. The hypothesis of McConnell (17) that misfits in the ordered structure of the triplet exciton systems are responsible for the paramagnetic impurities observed ($S=\frac{1}{2}$) is lent support by these observations: (a) CHT in thiourea inclusion compound self anneals rapidly* while CHT in naphthalene is extremely stable (b) CHT radicals are formed rapidly up to a certain maximum concentration in the inclusion compound while CHT is still being formed in naphthalene after 100 times longer irradiation. An explanation for these observations is that radicals are only formed at misfits at room temperature and once formed they diffuse via reaction until two CHT radicals meet and react to form bitropyl again.

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*In cycloheptatriene-thiourea inclusion compound. The bitropyl compound has not yet been checked for this.

In conclusion, it must be noted that because of the large change in nuclear configuration during the singlet-triplet transition the mobility of these excitons must be severely limited.

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