cyclic, triply conjugated system, has the highest value. On the other hand, estrone (Fig. 11) with an endocyclic, triply conjugated system in Ring I has a contrastingly low absorption intensity. In general, the type of linkages which produces the highest absorption are the conjugated double bond, and the double bond in conjugation to a keto, hydroxy, or other polar grouping. Compounds having both endocyclic and exocyclic unsaturation produce high extinction coefficients (see 7-keto-cholesterilene, and 7-keto-cholesterol (Fig. 3)). The influence of exocyclic changes have little effect in the absence of endocyclic unsaturation, while endocyclic unsaturation in the absence of exocyclic groupings produces a spectrum of rather high intensity (see cholesterilene, Fig. 6). Generally, in a conjugated double bond system wherein there is one center of electronic interaction a single narrow absorption band is exhibited while a system having two or more locations of electron concentration exhibits more than one maximum. Comparing the antimony trichloride spectra of 7-dehydrocholesterol and ergosterol (Fig. 3) the difference apparently is due to the side chain double bond of ergosterol. 7-Dehydrocholesterol gives a single strong maximum, due to the single conjugated system in Ring II, while ergosterol with electronic interaction between the side chain and Ring II give two prominent bands. Conversely, calciferol (Fig. 8) with a double bond in the side chain gives a single absorption maximum. Possibly there is no interaction between the semicyclic, triply conjugated system in Ring II and the side chain double bond of calciferol. An interesting analogy exists in the comparison of the ultraviolet absorption of ergosterol and calciferol.[8]

The nature of antimony trichloride reaction on a sterol was assumed (in the initial stages of this work) to be one of dehydration with subsequent shifting of double bonds, and possible introduction of an additional double bond. Preliminary experiments on the isolated reaction products of cholesterol, however, seem to indicate a cyclization product, probably forming a dicyclopentanoperhydrophenanthrene entity. A continuation of studies on this phase, as well as systematic investigations of a series are necessary before definite conclusions may be drawn.

Acknowledgment.—The writer wishes to express his appreciation to Sereck H. Fox for his criticism of this manuscript, and is very grateful to Gerard A. Fleisher for his interest and invaluable suggestions as well as for supplying most of the compounds investigated.

Summary

The absorption spectra data of the antimony trichloride reaction products of thirty-four steroids are presented. Absorption curves are shown for fourteen representative compounds in the region from 310 to 700 mμ. The data indicate that the spectra are characteristic for specific molecular groupings or combination of groupings in the molecule. Generalizations of the influence of various groupings in the steroid molecule on the resulting spectra are summarized. The analysis of the data obtained from the spectra would indicate that the latter are particularly helpful in following the progress or change in a molecule during synthesis, degradation, or in its quantitative analysis for purity and concentration.

DETROIT, MICHIGAN RECEIVED FEBRUARY 24, 1948

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[8] H. Dannenberg, *Abhandl. preuss. Acad. Wiss., Math. naturw. Klasse*, No. 21 (1939).

[CONTRIBUTION FROM MASSACHUSETTS INSTITUTE OF TECHNOLOGY, AND HARVARD UNIVERSITY]

The Microwave Spectra of CH_3NCS and CH_3SCN[1]

BY C. I. BEARD[2] AND B. P. DAILEY[3]

Introduction

The use of microwave absorption spectroscopy in determining the structure of linear and symmetric top molecules is now well established. The application to asymmetric molecules, although of much importance in broadening the scope of the techniques, has been very slow because of the complexity of the spectra which are observed. These complexities arise not only from the pattern (or lack of one) of rotational energy levels for the asymmetric rotor, but from nuclear quadrupole coupling, rotational-vibrational interaction, internal free or hindered rotation, and from experimental difficulties in observing spectra in the microwave region. All of these complications, except the last, are potential sources of useful information provided an analysis can be carried out. The natural procedure would seem to be to select molecules for study, to begin with, which would exhibit only one or two of these complications. As an example sulfur dioxide,[4] for whose spectrum a preliminary analysis has appeared, has no quad-

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[1] The research reported in this paper was made possible through support extended to B. P. Dailey, Harvard University, by the Navy Department (Office of Naval Research) under Office of Naval Research Contract N5ori-76 and C. I. Beard, Massachusetts Institute of Technology, under Joint Service Contract W-36-039sc-32037.

[2] Present address: Magnolia Petroleum Company, Field Research Laboratories, Dallas, Texas.

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[4] B. P. Dailey, S. Golden and E. B. Wilson, Jr., *Phys. Rev.*, **72**, 871 (1947).

rupole interactions (except in molecules involving S^{33}), no internal rotation, and possesses a readily observable spectrum in the microwave region.

In this paper results of the investigation of the microwave spectra of the slightly asymmetric tops, methyl isothiocyanate (CH_3NCS) and methyl thiocyanate (CH_3SCN) will be presented. These are members of an interesting class of asymmetric molecules possessing internal rotating groups. Other members of this class whose microwave spectra have been studied are CH_3NO_2,[5] CH_3NH_2,[6] and CH_3OH.[6,7] CH_3NCS would seem to be a favorable case for analysis since it has an easily observable spectrum in a convenient frequency range, has a negligible quadrupole coupling, and should be only slightly asymmetric. *In addition the approximate dimensions of the* NCS group are known from the microwave study of HNCS.[8]

Experimental Details

The CH_3NCS absorption spectrum has been studied in the frequency range from 20 to 30 kmc. using the Stark modulation spectrometer previously described.[9] The apparatus, shown in block diagram form in Fig. 1, used a waveguide absorption cell ten feet in length with a 100 kc./s. square wave Stark field. The CH_3NCS was an Eastman Kodak Co. product used without further purification.

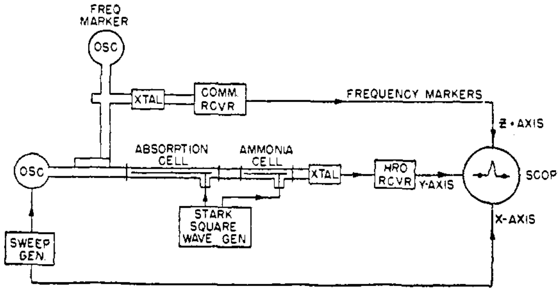

Fig. 1.—Arrangement of components in the microwave spectrometer.

With 100 v./cm. Stark field modulation and a vapor pressure ~0.05 mm. more than 29 CH_3NCS absorption lines were found in the region from 19,440 to 29,800 mc./s. (Fig. 2 and Table I). Frequencies in most cases were determined using lines of the $N^{14}H_3$ and $N^{15}H_3$ inversion spectrum as secondary standards, measuring frequency differences by the method of Good and Coles.[10]

TABLE I

ASSIGNMENT OF LINES IN THE ROTATIONAL SPECTRUM OF CH_3NCS

ν mc.	Relative intensity	Assignment
		$J = 3 \rightarrow 4$ transition
19700*	5	CH_3NCS^{34}; degenerate line, ground state
19929*	1	CH_3NCS^{34}; degenerate line, J
20020*	<1	
20140	10	CH_3NCS: $+3_{1,3} \rightarrow 4_{1,4}$ ground state
20216	100	CH_3NCS; degenerate line, ground state
20230	<1	
20241	7	CH_3NCS; degenerate line, E ?
20350	20	CH_3NCS; degenerate line, D
20413	<1	
20443	40	CH_3NCS; degenerate line, J
		$J = 4 \rightarrow 5$ transition
24143*	<1	$C^{13}H_3NCS$; degenerate line, ground state
24609*	5	CH_3NCS^{34}; degenerate line, ground state
24824	1	
24910	2	CH_3NCS^{34}; degenerate line, J
24930*	<1	CH_3NCS^{33}: degenerate line, ground state
24971*	1	
25002*	<1	$CH_3NC^{13}S$; degenerate line, ground state
25077*	1	
25100*	<1	
25161	<1	
25195	10	CH_3NCS; $4_{1,4} \rightarrow 5_{1,5}$, ground state
25269	100	CH_3NCS; degenerate line, ground state
25306	7	CH_3NCS: degenerate line, E ?
25333	10	CH_3NCS; $4_{1,3} \rightarrow 5_{1,4}$ ground state
25390	<1	
25409*	1	
25442	25	CH_3NCS; degenerate line, D
25550	40	CH_3NCS; degenerate line, J
25653*	<1	CH_3NCS: $4_{1,3} \rightarrow 5_{1,4}$, J
		$J = 5 \rightarrow 6$ transition
29700		CH_3NCS^{34}; degenerate line, ground state

The frequencies of the lines marked by asterisks in Table I were determined only by cavity wavemeter readings. The approximate relative intensities reported represent observed signal strengths at the same power level incident on the terminal crystal detector. These relative intensities are comparable only within each group of lines and are not true relative intensities since they neglect the dependence upon the Stark effect of each line. Furthermore saturation effects tend to increase the apparent relative intensity of the weaker lines.

Theoretical Spectrum

The analysis of the observed spectrum may be most conveniently discussed by setting up a probable structure for the molecule, calculating a theoretical spectrum and comparing with observed results. In view of the microwave data on HNCS, CH_3NCS can with some confidence be pictured as being a resonance hybrid of the three structures shown in Fig. 3. If it is assumed that the structure of the NCS group suffers no major changes in

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(5) B. P. Dailey and E. B. Wilson, Jr., paper presented at regional meeting of the American Physical Society, Amherst, Mass., May 31, 1947.

(6) W. D. Hershberger and J. Turkevitch, *Phys. Rev.*, **71**, 554 (1947).

(7) B. P. Dailey, *ibid.*, **72**, 84 (1947).

(8) C. I. Beard and B. P. Dailey, *J. Chem. Phys.*, **15**, 762 (1947).

(9) R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.*, **71**, 562 (1947).

(10) W. E. Good and D. K. Coles, *ibid.*, **71**, 383 (1947).

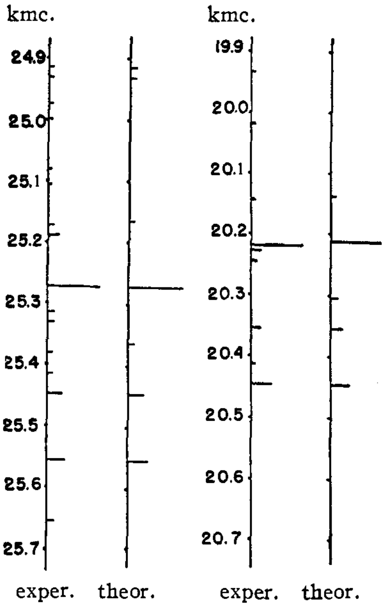


Fig. 2.—The experimental and calculated spectrum of CH_3NCS in the microwave region.

going from the acid to the ester, and the dimensions of the methyl group are taken from the recent accurate work on the methyl halides[11] only a value for the CH_3–N–C angle need be chosen for a complete molecular model. For a first approximation the H–N–C angle could be used although it has been determined only roughly. The N–C distance in HNCS indicates a predominance of the structure involving the N≡C bond and suggests that an angle greater than the average for the resonating structures, 130°, may be the correct one. For the present purpose an angle of 142° has been chosen. The influence of hyperconjugation on the CH_3–$^+$N≡C–S^- structure might lengthen the N–C bonds and shorten the CH_3–N bond but should leave the angle unchanged. The structure illustrated in Fig. 4 should roughly approximate the true molecular configuration and permit calculation of a theoretical spectrum correct in broad outline.

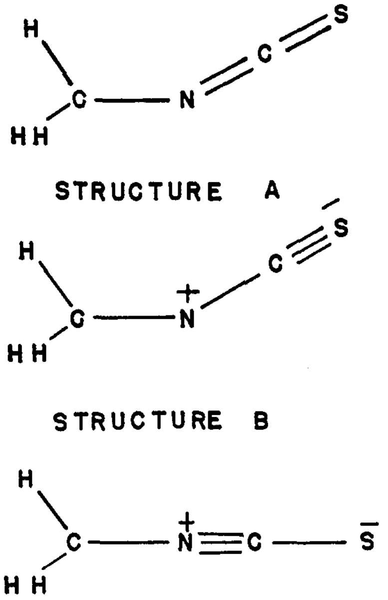
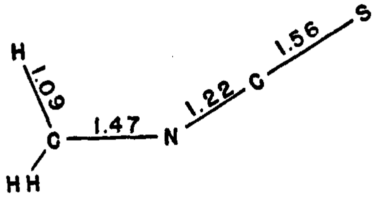


Fig. 3.—Resonating structures for CH_3NCS.



H–C–N angle 109°
C–N–C angle 142°

Fig. 4.—Approximate molecular configuration of CH_3NCS:

I_A, 10.72 × 10^{-40} g. cm.^{2}	A, 2.61 cm.$^{-1}$
I_B, 329.34	B, 0.08498
I_C, 334.85	C, 0.08358

Using the formula given by Mecke[12] for the energy levels of a slightly asymmetric rotor (which, in view of the near degeneracy of the rotational constants B and C, should apply in this case)

$$F(J,K)\text{ cm.}^{-1} = {}^1/_2(B + C)J\,(J + 1) + [A - {}^1/_2(B + C)]K^2$$

where $A = h/8\pi^2cI_A$, $B = h/8\pi^2cI_B$, $C = h/8\pi^2cI_C$, the following formulas for observed frequencies may be obtained: For

$$\Delta J = +1,\ \Delta K = 0$$
$$\nu\text{cm.}^{-1} = (B + C)(J + 1)$$

For

$$\Delta J = 0,\ \Delta K = +1$$
$$\nu\text{cm.}^{-1} = [A - {}^1/_2(B + C)(2K + 1)$$

Using the calculated rotational constants based on the approximate molecular model, spectral lines would be predicted at the frequencies given in Table II. An inspection of this table permits the widely spaced groups of lines at 20,500 and 25,000

TABLE II

CALCULATED ROTATIONAL SPECTRUM FOR CH_3NCS CONSIDERED AS A NEARLY SYMMETRIC ROTOR

J	K	J'	K'	ν, cm.$^{-1}$	ν, mc./s.
0	0	1	0	0.16856	5,053
1	1	2	1	.33712	10,106
2	2	3	2	.50568	15,159
3	3	4	2	.67424	20,212
4	4	5	4	.84280	25,265
5	5	6	5	1.01136	30,319
0	0	0	1	2.5257	75,716
1	1	1	2	7.5772	227,148

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[11] J. W. Simmons, W. Gordy and A. G. Smith, *Phys. Rev.*, **74**, 243 (1948).

[12] R. Mecke, *Z. Physik*, **81**, 313 (1933).

mc. to be identified as arising from the parallel type transitions $J = 3 \rightarrow 4$ and $J = 4 \rightarrow 5$. Detailed analysis to be presented later indicates that the lines at 29,800 are the beginning of the $J = 5 \rightarrow 6$ group. On the basis of these simple considerations, however, each of these transitions should consist of but a single line. Since there are more than 19 components in the $J = 4 \rightarrow 5$ group alone some explanation must be found for the extra lines.

Removal of Degeneracies

Considering the various complicating factors in turn, the removal of degeneracies known to exist in the pattern of symmetric rotor energy levels by the asymmetry of the molecule and by the modulating field will be taken up first. Each J level in the symmetric rotor is made up of $2J + 1$ degenerate levels corresponding to the individual values of K. In turn each JK level is made up of $2J + 1$ levels, degenerate in the absence of an external field, corresponding to the individual values of the quantum number M. In the specific case of a molecule having the structure indicated in Fig. 4 the K degeneracy is at least partially removed by the molecular asymmetry. The transition frequencies for such an asymmetric rotor have been calculated using third order perturbation theory and the coefficients tabulated by King, Hainer and Cross,[13] and are given in Table III. The single line predicted above for the $J = 4 \rightarrow 5$ transition, for example, has been replaced by a pattern of three lines. The lines corresponding to (in the KHC notation) the $4_{1.4;-3} \rightarrow 5_{1.5;-4}$ and $4_{1.3;-2} \rightarrow 5_{1.4;-3}$ transitions have split, not quite symmetrically, some 100 mc. away, on either side of the degenerate line.

TABLE III

CALCULATED ROTATIONAL SPECTRUM FOR CH_3NCS CONSIDERED AS AN ASYMMETRIC ROTOR

Transition	ν, mc.
$3_{0.3;-3} \rightarrow 4_{0.4;-4}$	20.215
$3_{1.3;-2} \rightarrow 4_{1.4;-3}$	20,131
$3_{1.2;-1} \rightarrow 4_{1.3;-2}$	20.297
$3_{2.2;0} \rightarrow 4_{2.3;-1}$	20.215
$3_{2.1;+1} \rightarrow 4_{2.2;0}$	20,216
$3_{3.1;+2} \rightarrow 4_{3.2;+1}$	20,215
$3_{3.0;+3} \rightarrow 4_{3.1;+2}$	20,215
$4_{0.4;-4} \rightarrow 5_{0.5;-5}$	25,262
$4_{1.4;-3} \rightarrow 5_{1.5;-4}$	25.158
$4_{1.3;-2} \rightarrow 5_{1.4;-3}$	25,364
$4_{2.3;-1} \rightarrow 5_{2.4;-2}$	25,265
$4_{2.2;0} \rightarrow 5_{2.3;-1}$	25.266
$4_{3.2;+1} \rightarrow 5_{3.3;0}$	25.265
$4_{3.1;+2} \rightarrow 5_{3.2;+1}$	25.265
$4_{4.1;+3} \rightarrow 5_{4.2;+2}$	25,265
$4_{4.0;+4} \rightarrow 5_{4.1;+3}$	25.265

Since the spectrometer employs an applied electric field for modulation, the spectrum actually observed is complicated by the presence of lines corresponding to the individual M values. The experimental arrangement is such that the electric radiation vector and the applied electric field are parallel (except for negligible fringing effects near the edges of the waveguide absorption cell) and the selection rule $\Delta M = 0$ is obeyed. Analysis of this pattern of Stark components would allow calculation of the component of dipole moment along the approximate figure axis of the molecule but unfortunately the complexity of the not very intense spectrum was such that an analysis has not been carried out. In the reported spectrum Stark components have been omitted by eliminating all lines whose frequency varied with the electric field.

Centrifugal Distortion

The foregoing calculations were based on the assumption that the molecule was rigid. The actual molecule is subject to centrifugal distortion which will have an effect on the pattern of rotational energy levels. Slawsky and Dennison[14] give an expression for the energy levels of a non-rigid symmetric rotor

$$F(J,K) = BJ(J + 1) + (A - B)K^2 - D_J J^2(J + 1)^2 - D_{JK}J(J + 1)K^2 - D_K K^4$$

which leads to an expression

$$\nu = 2B(J + 1) - D_J(J + 1)^3 - D_J'(J + 1) + D_{JK}K^2(J + 1)$$

for the frequencies of the rotational transitions Slawsky and Dennison give the following calculated values of the constants for the case of CH_3Cl

$D_J = 0.0036$ mc/s.
$D_J' = 0.0414$ mc/s.
$D_{JK} = 0.4020$ mc/s.

Gordy, Simmons, and Smith[9] report an experimental value of D_{JK} for CH_3Cl of 0.19 mc. The term involving D_{JK} is much the largest and should lead to a separation between the $K = 0$ and $K = 4$ components of the degenerate transition of as much as 15 mc. In the experimental spectrum there is considerable evidence of fine structure on the high frequency side of the degenerate line but interference from the pattern of Stark components has prevented any accurate measurement of this centrifugal splitting. The term involving D_J will cause deviations from the frequencies predicted using a linear relation between ν and $J(J + 1)$. The example of CH_3Cl makes it seem probable that this effect would be unobservable with the precision of frequency measurement available in this study.

Excited Vibrational States

The interaction of vibration and rotation has so far been neglected. The rotational constant B (and A and C as well) actually has different values in the different vibrational states. This de-

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(13) G. W. King, R. M. Hainer and P. C. Cross, *J. Chem. Phys.*, **11**, 27 (1943).

(14) Z. I. Slawsky and D. M. Dennison, *J. Chem. Phys.*, **7**, 509 (1939).

pendence of B on the vibrational quantum numbers is indicated by the following formula, taken from Herzberg[15] where the α_i are small compared

$$B_{[v]} = B_e - \sum_i \alpha_i^B (v_i + d_i/2)$$

to B_e, which is the rotational constant for the equilibrium position. d_i is the degree of degeneracy of the vibration v_i. The summation extends over all vibrations. The constants α_i are usually positive for the non-degenerate vibrations of linear molecules, but may be positive or negative for the degenerate vibrations.

No complete vibrational study and resulting assignment of fundamentals has yet been published for CH_3NCS. However, Goubeau and Gott[16] have determined the stretching frequencies for the linear portion of the molecule and Eyster and Gillette[17] have made vibrational assignments for similar molecules including CH_3NCO. The approximate vibrational frequencies listed in Table IV should then be at least of the correct order of magnitude. The Boltzmann factors computed from these frequencies indicate roughly the expected ratio of relative intensities of spectral lines due to the same transition for molecules in the ground and excited vibrational states.

TABLE IV

APPROXIMATE VIBRATION FREQUENCIES FOR CH_3NCS

Series	CH_3NCO ω cm.$^{-1}$	CH_3NCS ω cm.$^{-1}$	CH_3NCS $e^{-h\nu/kT}$
A	870	850	0.0166
B	2232	2162	< .0001
C	1412	1087	.0052
D	353	300	.2340
E	652	600	.0550
	607	550	.0699
F	2994	3000	< .0001
	2951	2950	< .0001
G	1453	1450	.0009
		1440	.0009
H	1377	1375	.0014
I	1181	1200	.0030
	1107	1100	.0049
J	?	200	.2982

The vibrations of series A correspond to CH_3–N stretching frequencies. Series B and C are stretching frequencies localized within the linear portion of the molecule. B is the N–C stretching and C the C–S stretching frequencies in CH_3NCS. The D vibration corresponds to the bending of the CH_3–N bond against the linear group. The E vibrations are the perpendicular bending vibrations of the linear group.

The vibrations F through H are the well known internal vibrations of the methyl group and the I vibrations correspond to the rocking frequencies of this group. The torsional oscillation frequency J requires further discussion.

Internal Rotation

The features of the spectrum due to the internal rotation of the methyl group and isothiocyanate group independently about the molecular axis will depend upon the height of the barrier hindering the rotation. If the barrier is of a comparable (although probably somewhat smaller) magnitude to that in the roughly similar case of methanol[18] an appreciable number of molecules will occupy the first excited torsional vibration level. Indeed, if the figure 200 cm.$^{-1}$ for the height of this excited state above the ground level listed in Table IV is correct a line in the observed spectrum due to the second excited state might well appear. In methanol the ratio of populations for the ground state and first excited state of torsional vibration is 0.18; in the case of CH_3NCS this ratio would probably be somewhat larger.

The torsional vibrational states, according to the analysis of the methyl alcohol problem presented by Koehler and Dennison,[18] are actually made up of a number of sublevels with a spread in energy which increases with the torsional vibration quantum number. In general there are three sublevels for each permitted K value although certain degeneracies occur. For methyl alcohol the spread of the energy levels for the first excited state has been calculated to be 33 cm.$^{-1}$. Since this spread varies inversely with the barrier height an even wider separation of levels would be expected for CH_3NCS. It is difficult to predict whether the first excited torsional state will give rise to a single broad line in the pure rotation spectrum or will have a resolvable structure.

For low values of the barrier height, and in any case for torsional vibration states higher than the second or third, the internal rotation would be essentially free. If we apply the analysis of Koehler and Dennison[18] (which should fit only roughly because of the considerable asymmetry of the NCS group) the following expression for the frequencies of the lines in the $\Delta J = 0$ series may be used

$$\lambda = A_1 - B - 2BK + 2A_1K_1$$

A_1 is the rotational constant for the NCS group about the molecular axis (not the symmetry axis of the methyl group). Using the rotational constants given in Fig. 4 and a minimum value of A_1 of 3.0 cm.$^{-1}$ the frequencies for this series were calculated. All lie outside the experimental frequency range for this investigation.

A limit to the complexity introduced into the observed spectrum by excited vibrational states is set only by the available sensitivity of the spectrometer. If the observed spectrum is limited to those lines whose apparent intensity is at least

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[15] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 370.

[16] J. Goubeau and O. Gott, *Ber.*, **73B**, 127 (1940).

[17] E. H. Eyster and R. H. Gillette, *J. Chem. Phys.*, **8**, 369 (1940).

[18] J. S. Koehler and D. M. Dennison, *Phys. Rev.*, **57**, 1006 (1940).

0.005 of that for the most intense line in the spectrum the Boltzmann factors listed in Table IV should permit selection of the vibrations whose first excited states might give rise to lines. On this basis the most intense of the excited vibration lines should be due to the torsional vibration J. Next most intense would be the line corresponding to the first excited state of the CH_3–N bending vibration, D. Following in order of intensity would be the second excited levels for these two vibrations and the first excited levels for the nearly degenerate bending modes of the NCS group, E. Finally a line due to the first excited level for the CH_3–N stretching vibration, A, might be seen. The α's for these vibrational states cannot be easily calculated so that the lines due to excited vibrational states must be identified from their intensities and from the change of intensity with temperature. The experimental measurement of temperature coefficients of intensity was made rather difficult by the small temperature range over which measurements could be made for this molecule and with the present equipment. The rough values obtained, however, definitely serve to establish several of the fairly intense lines as being due to excited vibrational states.

Isotopic Spectra

There should be, of course, separate and easily resolvable microwave spectra for each of the different isotopic varieties of the CH_3NCS molecule. The relative intensities of lines due to the more abundant naturally occurring CH_3NCS molecules have been calculated and are given in Table V.

TABLE V

RELATIVE ABUNDANCE OF ISOTOPIC VARIETIES OF CH_3NCS

Molecule	Relative abundance
$C^{12}H_3N^{14}C^{12}S^{32}$	100.00
$C^{12}H_3N^{14}C^{12}S^{34}$	4.40
$C^{12}H_3N^{14}C^{12}S^{33}$	0.76
$C^{13}H_3N^{14}C^{12}S^{32}$	1.08
$C^{12}H_3N^{14}C^{13}S^{32}$	1.08
$C^{12}H_3N^{15}C^{12}S^{32}$	0.38

If the same range of relative intensities is used here as was proposed earlier in the discussion of excited vibrational states any or all of these molecules might give rise to observable spectra. It is even probable that for the molecule involving S^{34} lines due to both the ground and excited vibrational states would be seen.

Nuclear Quadruple Coupling

Two of the nuclei which are concerned in the CH_3NCS molecular species have nuclear quadrupole moments—N^{14} and S^{33}. In the latter case the intensity of the main transition must be so low that the quadrupole fine structure would be unobservable. For N^{14}, intensities of the fine structure components might be sufficient but it is doubtful that the spectrometer was operated with sufficient resolving power to separate the individual lines. In the closely similar case of N in CH_3NC[6] the quadrupole splitting has been reported as less than 1 mc. Line widths in this study were considerably larger than this figure. Lines were, in fact, unusually broad although extra width seems to be a feature of the microwave rotational spectral lines of symmetric rotors possessing large dipole moments.

Other Asymmetric Rotor Transitions

In considering the molecule as an asymmetric rotor certain transitions become possible other than the ones so far dealt with, which correspond to the parallel type $\Delta J = 1$, $\Delta K = 0$ transitions of the prolate symmetric rotor, and in the KHC notation[19] are described as $ae_{R_{0,1}}$ or $ao_{R_{0,1}}$. For the most part, however, the intensities of other types of "a" transitions may be shown to be too small to be detected with the present equipment for all reasonable values of the asymmetry parameter κ. The only other "*a*" transition which might be observable are the $ao_{Q_{0,1}}$-transitions between the split components of each K level. Very high J values would be required to bring the frequencies of such lines into the observed region so that the resulting Boltzmann factors would reduce their intensities to a rather small figure. Such transitions would be so widely spaced that at most they could account for only two or three lines in the entire experimental frequency range.

Since there is no component of the dipole moment along the I_C axis (perpendicular to the C–N–C–S plane) "*c*" type transitions will have zero intensity. While a small component of the dipole moment does exist along the I_B axis, the intensities of "*b*" type transitions would be quite small since the intensity is proportional to the square of the dipole moment component. There are a number of lines of low intensity in the observed spectrum which have not been accounted for (as well as some for whose assignment there is at least a reasonable doubt), so this possibility cannot be completely ruled out.

Analysis of Observed Spectrum

An analysis of the observed spectrum has been made in the light of the discussion above and the results are presented in Table I. The theoretical spectrum, calculated using the molecular model described in Fig. 4, and compared to the experimental spectrum in Fig. 2, reproduces the general features of the experimental spectrum quite well. The features of this spectrum which are advanced with the most confidence are the following: The average rotational constants, $^1/_2(B + C)$, for CH_2NCS in the ground vibrational state have the value indicated in Table VI. Certain of the lines in different transition groups reveal by the ratio of their frequencies that they correspond to the

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(19) P. C. Cross, R. M. Hainer and G. W. King, *J. Chem. Phys.*, **12**, 210 (1944).

same average rotational constant, which is different from the value assigned the most abundant isotopic variety in the ground vibrational state.

TABLE VI

Molecule	ν, mc.	$^1/_2(B + C)$, cm.$^{-1}$	Transition	Vib. state	$I_{av.}$, g. cm.^{2}
CH_3NCS	20216	0.084295	$J = 3 \rightarrow 4$	Ground	332.01 × 10^{-40}
	25269	.084292	$J = 4 \rightarrow 5$	Ground	332.02
	20443	.085241	$J = 3 \rightarrow 4$	*J*	328.33
	25550	.085223	$J = 4 \rightarrow 5$	*J*	328.40
	20350	.084854	$J = 3 \rightarrow 4$	*D*	329.83
	25442	.084869	$J = 4 \rightarrow 5$	*D*	329.77
CH_3NCS^{34}	19700	.082144	$J = 3 \rightarrow 4$	Ground	340.71
	24609	.082090	$J = 4 \rightarrow 5$	Ground	340.93
	29540	.082116	$J = 5 \rightarrow 6$	Ground	340.82
	19929	.083099	$J = 3 \rightarrow 4$	*J*	336.79
	24910	.083094	$J = 4 \rightarrow 5$	*J*	336.81

The details of the assignment of these rotational constants to different isotopic varieties of the molecule in different vibrational states depends upon measurements of relative intensity and calculations of isotopic frequency shifts. The relative intensities are highly approximate because of difficulties encountered in their measurement. The calculated frequency shifts, of course, depend upon the assumed molecular model. However, in the case of the lines assigned to the first excited torsional vibration level the intensities are so large as to rule out most other possible assignments. For the lines assigned to CH_3NCS^{34} both the frequency shifts and the intensities are of the right order of magnitude and their agreement tends to support the conclusion. The assignment of the next most intense set of lines to the first excited state of the CH_3–N bending mode seems reasonable since in the vibrational assignment for similar molecules this is much the lowest lying vibration exclusive of torsion. The assignment of lines to the nearly degenerate bending modes of the NCS group is much more doubtful but has been made simply on the basis of the relative intensities. Because of the complexity of the spectrum the interesting question of the effects of the near degeneracy and slight asymmetery on what would be *l*-type doubling in a linear molecule has not been pursued.

Because of the uncertainty in the degeneracy of the lines ascribed to the first excited torsional vibration level the assignment of the lines in the neighborhood of 25500 mc. is rather tentative. It is perhaps possible that this group of lines is made up of the resolved components of the degenerate line.

The designation of certain of the lines as components of the degenerate main transition split out by the molecular asymmetry is somewhat difficult because their spacing is quite sensitive to small changes in the rotational constants and their intensities are low enough to permit confusion with the excited vibrational lines. The spacing of the lines should be nearly symmetric about the degenerate line and should be greater for the $J = 4 \rightarrow 5$ transition than for $J = 3 \rightarrow 4$. The relative intensities should be in the calculated ratio. Most of these requirements are at least roughly met by the assignment given above.

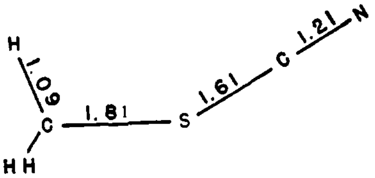
CH_3SCN Spectrum

With the same Stark modulation apparatus, the region from 20,000 to 30,000 mc. was searched for lines of methyl thiocyanate. The observed spectrum was similar in many respects to that for the tautomeric ester although, of course, occurring at different frequencies. Again the spectrum consisted of complex groups of lines. However, for methyl thiocyanate the intensities were so low that only the strongest lines could be properly studied. The two strongest lines, which by analogy with the tautomeric ester would be assigned to the degenerate transition of the ordinary isotopic form of the molecule, were found to have the frequencies given in the table.

Frequency, mc.	Transition	Average rotational constant, cm.$^{-1}$
22,680	$J = 3 \rightarrow 4$	0.09457
28,380	$J = 4 \rightarrow 5$	.09467

The frequencies were determined using a cavity wavemeter and are accurate only to ± 10 mc.

The frequency ratio of these lines enables them to be identified as $\Delta J = 1$, $\Delta K = 0$ transitions of a slightly asymmetric rotor involving the *J* values listed above. This conclusion is supported by callations based on various probable structures of the CH_3SCN molecule. By assuming probable values of the interatomic distances, the C–S–C angle corresponding to moments of inertia resulting from the observed value of $^1/_2(B + C)$ could be calculated. The CH_3SCN structure shown in Fig. 5 is the one consistent with the above considerations. In order to determine the structure completely from the spectrum, independent of the above assumptions, spectra for several different isotopic varieties of the molecule, probably synthesized from enriched material, would have to be observed.



H–C–S angle 109°
C–S–C angle 142°

Fig. 5.—Approximate molecular configuration of CH_3SCN.

Summary

Measurements of the pure rotational spectra of CH_3NCS and CH_3SCN have been made in the frequency range from 20,000 to 30,000 mc. Experimental techniques used and the interpretation of the spectra of these molecules are discussed. A theoretical spectrum for CH_3NCS has been set up and the complicating effects of the removal of de-

generacies by asymmetry and by an external electric field, of centrifugal distortion, of the presence of excited vibrational states, of internal rotation, of isotopic varieties of the molecule, of nuclear quadrupole coupling, and of other allowed asymmetric rotor transitions are calculated. There is good general agreement between the theoretical and observed spectra for CH_3NCS. The spectrum of CH_3SCN was too weak for detailed analysis but values of the average rotational constant $^1/_2 (B + C)$ are presented.

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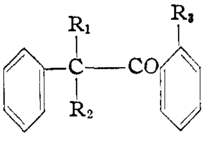
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Steric Hindrance in the Stobbe Condensation[1]

BY MELVIN S. NEWMAN AND JACK LINSK[2]

The first step in the recently reported method for the synthesis of 1,2-benzanthracene[3] involves the Stobbe condensation (in 60% yield) of desoxybenzoin, I ($R_1 = R_2 = R_3 = H$), and methyl succinate. In order to apply this method to the synthesis of 1',9-dimethyl-1,2-benzanthracene,



we prepared, *o*,α-dimethyldesoxybenzoin, II ($R_1 = R_3 = CH_3$, $R_2 = H$) and attempted to condense it with ethyl succinate. In spite of numerous attempts including the use of potassium *t*-butoxide[4] in place of sodium ethoxide and the substitution of methyl succinate, succinic anhydride, and *n*-methylsuccinimide for ethyl succinate, we were entirely unsuccessful. To test the suggestion that enolization of the ketone[5] might be responsible for this failure to condense, we prepared *o*,α,α-trimethyl-desoxybenzoin, III ($R_1 = R_2 = R_3 = CH_3$), and attempted the reaction, but without success. Hence it appeared that steric factors were involved.

Accordingly we prepared α-methyldesoxybenzoin, IV ($R_1 = R_3 = H$, $R_2 = CH_3$), α,α-dimethyldesoxybenzoin, V ($R_1 = R_2 = CH_3$, $R_3 = H$), and 2,5-dimethylphenyl benzyl ketone, VI (a compound analogous to *o*-methyldesoxybenzoin [$R_1 = R_2 = H$, $R_3 = CH_3$] but easier to prepare) and have tested these under similar conditions in the Stobbe reaction. All of these attempts failed except that with IV, which gave the expected product in about 60% yield. Thus, from a comparison of the reactions involving ketones IV and VI, it appears that the substitution of one methyl group in the ortho position of the phenyl group adjacent to the carbonyl is more effective in hindering reaction than the substitution of a methyl group in the methylene group. Substitution of a second methyl group in the methylene group (ketone V) effectively hinders reaction.

Experimental[6]

2-Phenyl-1-*o*-tolyl-1-propanol.—A solution of 386 g. (2.87 mole) of hydratropaldehyde[7] in 600 cc. of dry ether was added dropwise during two hours to a well stirred solution containing the Grignard reagent prepared from 835 g. (3.83 mole) of *o*-iodotoluene in two liters of dry ether. After decomposition of the reaction mixture with iced hydrochloric acid, the alcohol was obtained as a colorless oil, b. p. 149–150° at 2 mm., in 65% yield. The *p*-nitrobenzoate melted at 112.1–113.4° after three recrystallizations from methanol.

Anal.[a] Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 85.0; H, 8.1. Calcd. for $C_{23}H_{21}O_4N$: N, 4.0. Found: N, 4.2, 4.0.

***o*,α-Dimethyldesoxybenzoin, II.**—In all attempts to oxidize the above alcohol using chromic oxide, potassium dichromate and sulfuric acid, or nitric acid, considerable cleavage into acetophenone and *o*-toluic acid occurred. In the best experiment 220 g. (0.98 mole) of the alcohol was added during ten minutes to a well-stirred two phase system composed of 100 cc. of benzene and a solution of 200 g. of potassium dichromate in 900 cc. of water and 90 cc. of concentrated sulfuric acid. The temperature slowly rose to 54° but did not go higher. After stirring for twelve hours, during which time the temperature fell to room, the reaction products were taken into ether. The acid was removed by an alkaline wash and the ketone was obtained in 65% yield as a colorless oil, b. p. 120–124° at 1 mm., which soon crystallized. A sample crystallized from methanol melted at 54.4–55.5°. The 2,4-dinitrophenylhydrazone formed small yellow needles, m. p. 136.0–137.0° after several crystallizations from ethyl acetate and from chloroform-alcohol. In all attempts to effect a Stobbe condensation, the ketone was recovered in high yield.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found[a]: C, 85.7; H, 7.3. Calcd. for $C_{22}H_{20}O_4N_4$: C, 65.3; H, 5.0; N, 13.9. Found[c]: C, 65.2; H, 4.7; N, 13.5.

***o*,α,α-Trimethyldesoxybenzoin, III.**—Ketone II was methylated with potassium *t*-butoxide and methyl iodide[8] to yield III as a solid, m. p. 37–38°, in 92% yield. A sample recrystallized for analysis melted at 38.6–39.6°. We were unable to prepare a 2,4-dinitrophenylhydrazone, semicarbazone, or oxime of this ketone, or to secure any acidic material after attempted Stobbe condensations.[4]

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(1) The material herein presented is taken from the Ph.D. thesis of Jack Linsk, Ohio State University, June, 1948. Present address: Standard Oil Company of Indiana, Whiting, Indiana.

(2) Abbott Laboratories Fellow, 1947–1948.

(3) Newman and Hart, THIS JOURNAL, **69**, 298 (1947).

(4) W. S. Johnson, A. Goldman and W. P. Schneider, *ibid.*, **67** 1367 (1945).

(5) Private communication from Dr. W. S. Johnson, University of Wisconsin.

(6) All melting points corrected. Analyses marked [a] by the Oakwold Laboratories, Alexandria, Va., [b] by James Polglase, Ohio State University, and [c] by Mrs. Edith Klotz, Ohio State University.

(7) Obtained from the Van Ameringen-Haebler Co., 417 Rosehill Place, Elizabeth, New Jersey.

(8) W. S. Johnson, THIS JOURNAL, **65**, 1317 (1943).