COMPLEX FORMATION BETWEEN HETEROCYCLIC COMPOUNDS AND POLYNITRO BENZENE DERIVATIVES

by

KATHLEEN LENORE MCEWEN

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of

MASTER OF SCIENCE

in the Department of

CHEMISTRY

We accept this thesis as conforming to the standard required from candidates for the Degree of MASTER OF SCIENCE -

University of British Columbia

April 1953

Abstract

Complexes formed between heterocyclic compounds and polynitro benzene derivatives have been examined spectroscopically. It has been found that many complexes, when irradiated in the region of their charge-transfer absorption emit a short-lived radiation in the region of the heterocyclic triplet. There is some evidence for a radiationless transition from an excited, bonding charge-transfer state to the excited triplet level of the heterocyclic component.

ACKNOWLEDGMENT

I wish to express my sincere appreciation to Dr. C. Reid for suggesting and advising me in this research.

I should also like to acknowledge my indebtedness to the National Research Council of Canada for a studentship.

TABLE OF CONTENTS

INTRODUCTION -

,

page.	
-------	--

The Importance of Molecular Complexes 1
Simple Types of Molecular Complex 2
The Type of Bonding Responsible 3
The absorption Spectra of Complexes 8
Molecular Orbital Theory for Complexes 9
Phenomena not Immediately Explainable by Charge Transfer 12
Phenomena Explained by Complex Formation 13
Reason for present Investigation 15
A Review of Electronic Properties of Heterocyclics 15
Transitions Found in Heterocyclics 17

EXPERIMENTAL METHODS AND RESULTS -

Apparatus 2	1
Rrocedure 2	1
Results 2	4
ISCUSSION 3	9a
IBLIOGRAPHY 4	7
PPENDIX 5	1

COMPLEX FORMATION BETWEEN HETEROCYCLIC COMPOUNDS AND POLYNITRO BENZENE DERIVATIVES

Introduction

THE IMPORTANCE OF MOLECULAR COMPLEXES

The group of compounds known as molecular compounds or molecular complexes has become of great interest during recent years. From a theoretical standpoint alone, it is extremely important to understand the type of bonding involved in complex formation and the various energy relationships possible between the components of a complex. However, such knowledge would also add considerably to our understanding of many vitally important but complicated reactions in which complex formation is involved at some stage.

For instance, it has been suggested that photosynthesis may depend upon the formation of a loose complex between a chlorophyll molecule and a carbon dioxide molecule, in contact with a suitable enzyme. This might solve the problem of how the reaction forming glucose from carbon dioxide and water, which requires 112,000 calories per carbon dioxide molecule, can take place in a system absorbing only visible light. There may be a mechanism whereby a chlorophyll molecule could absorb three quanta of red light, which together would correspond to about 112,000 calories, and transfer them to one place where they would be available to the complexed carbon dioxide. Another biological problem, a partial solution to which may lie in increased knowledge of complex formation, is that of carcinogenesis. It has been found that aromatic carcinogens combine with desoxyribose nucleic acid in the cells, and it is possible that they may thus change the properties of the acid enough to cause chromosome aberrations. Furthermore, it is thought that certain compounds, such as caffein may be anitcarcinogenic, since they compete to complex the aromatic carcinogens.¹⁷

SIMPLE TYPES OF MOLECULAR COMPLEX

At the present stage of knowledge, perhaps the best way to gain an understanding of the very complicated systems discussed in the foregoing section, will be to turn to complexes between far simpler molecules and to review what is known of them.

Probably the best known of the organic molecular complexes is the familiar picrate or polynitrobenzene derivative formed by aromatic hydrocarbons.³¹ The instant deepening of colour observed when a solution containing a hydrocarbon is added to one containing a polynitro compound has been a source of interest for many years. Such complexes are also formed between certain quinones and aromatic hydrocarbons.⁵³

In all cases the stability of the complex increases with increasing deactivation of the nitro-compound ring, or of the quinone; accomplished, for example, by the addition

-2-

of more nitro or carboxy substituents to the former, and halogen substituents to the latter. In respect to the hydrocarbon component, however, stability is increased by activating the aromatic ring system; for instance, by methylation, or by extending the aromatic system over more rings.

Another interesting series of molecular complexes which have been examined quite thoroughly during the past few years, are those formed by halogen molecules and aromatic hydrocarbons; usually in a ratio of 1 : 1, although there is some evidence for 1 : 2 complexes.³⁸ The first evidence that complex formation of this type occurs was from low temperature phase diagrams, and from viscosity measurements.³⁹ More recently a number of investigators have examined the absorption peaks of these complexes and have found that, in analogy with the strong colour of the picrates, complex formation between a halogen molecule and a molecule of an aromatic hydrocarbon produces an absorption maximum that belongs to neither component. This new absorption band will be discussed in detail later.

THE TYPE OF BONDING RESPONSIBLE FOR COMPLEX FORMATION

Naturally much curiosity was aroused as to the type of bonding between these pairs of stable molecules. One of the earliest postulates in this connection was that of Weiss, that complexes of quinones or polynitro-compounds with aromatic hydrocarbons are simple ionic compounds, in which the hydrocarbon gives an electron to the more electropositive

-3-

nitro compound or quinone.⁶⁸ Weiss presented dipole moment data which indicated some such bonding mechanism.

Soon after this, Woodward, coming closer to the present idea of bonding in molecular complexes, suggested that an intermolecular semipolar bond might explain complex formation; that is, an arrangement such as $(\emptyset (NO_2)_3)^{\circ}$ $(Ar)^{\circ}.^{69}$

Dewar has pointed out that London dispersion forces may be used to account for complex formation between aromatic ring systems.²⁴ That is to say, the periodically varying electron densities on the two rings, the time averages of which are represented by the wave functions I_{1} and I_{2} , will synchronize with one another in such a way as to produce a net attraction. This attraction will be strong if it results in compensating for a net electropositivity of one ring system. For instance, consider a pair of compounds such as anthracene and s-trinitrobenzene. The π electron system of the s-trinitrobenzene ring is to some extent electropositive, because of the resonance effect of the nitro groups. The anthracene, on the other hand, has a readily polarizable // electron system, and may be visualized as ready to neutralize the positive charge on the s-trinitrobenzene ring. In a sense the latter may be called an electron acceptor, and the hydrocarbon a donor.49

Very recently, Mulliken put this idea of a partial transfer of an electron into a more exact mathematical form than is implicit in the descriptions of bonding given above. The details of this theoretical approach will be considered

-4-

in a subsequent section; but, in brief, the theory involves assuming a small amount of $\mathcal{O}(NO_3)^{\ddagger}$ - $(Ar)^{-}$ character in the wave function, in which electron transfer has occurred and the orbitals now containing only one electron overlap to form a covalent bond.

This modified Lewis acid-base theory has been borne out by a wealth of experimental evidence, mainly concerning halogen-benzene type complexes. For instance, toluene, m-xylene, and naphthalene form stronger complexes than does benzene, 2,5,6,8 , and it is known that the electron densities of the ring systems of the two former are higher than that of the benzene ring; while naphthalene, being much more polarizable than benzene,will also act more readily as an electron donor.

Turning now to the "acid" or acceptor molecule, we find that the strength of the complex increases in order $Cl_2 \leq SO_2 \leq$ $Br_2 \leq I_2 \leq ICI.^3$ This is what one would expect, at least for the series Cl_2 , Br_2 , I_2 ; for clearly the electron affinity, or tendency to become X_2^- will increase in going from Cl_2 to I_2 . The fact that ICl does not act like Br_2 in regard to strength of complex formation, as would be expected, must be explained by other factors.

It will be of use in visualizing the form of more complicated complexes, to consider the probable electronic structure of the benzene-iodine complex, and to see what factors are important in such a consideration.⁵⁰ The most probable form of the complex is that with the iodine molecule resting on the benzene molecule, its axis parallel to one of the twofold axes

~5~

of the benzene ring, and its centre on the six-fold axis of the benzene. In this form the complex will have symmetry C_{2v} . We must now examine the molecular orbitals of benzene and of iodine (or I_2^-) under a perturbing field of symmetry C_{2v} . There are three # molecular orbitals in the ground state of benzene to be considered; while the 5p orbitals of the iodine atom combine to form six molecular orbitals of the

form shown in Fig. 1



<u>Fig. 1.</u> Schematic diagrams for the case of a perturbing field of C_{2v} symmetry with xy and yz as symmetry planes.

(a) Benzene - the relative sizes of the circles indicate the relative charge densities on each atom for that molecular orbital. Shaded circles indicate a positive wave function on the positive-z side of the benzene plane.

(b) Iodine - shaded portions indicate positive regions of the wave function, unshaded portions, negative. The y axis is the intermolecular axis. The inner nodes of the atomic orbitals are omitted.

The a_1 , b_1 , etc, refer to the symmetry species classifications of the orbitals. The f_{n} , refer to the 5p atomic orbitals parallel to the x, y, and z axes respect-In the ground state of iodine there are two electivelv. rons in each orbital except the last, which is strongly However, the ground state of I_2^- will have antibonding. one electron in the b₂ δ_{11} orbital, giving a ²B₂ state for I_2^- . Now since the ground state of the complex is required to have the symmetry l_{A_1} , the electron donated by the benzene will have to come from the orbital belonging to the symmetry species b_2 , so that the (benzene)^{*} will also be in its ${}^{2}B_{2}$ state. It will be seen that this arrangement will give excellent overlap of the two bonding orbitals of I_2^- and (benzene)⁺.

The symmetry requirements mentioned above will also hold for nitro-compound complexes as long as the complex has some overall symmetry. If it has not, then the same approximate symmetries must exist for the two complexing molecules in the region of their interaction at least. However, it is clear that such considerations will become quite complicated even in reasonably simple polynitrobenzene-hydrocarbon complexes.

THE ABSORPTION SPECTRA OF MOLECULAR COMPLEXES

As was mentioned earlier, both picrate-type complexes and halogen complexes show absorption bands which

÷7=

are peculiar to neither of the original components. The picrates have a long, continuous absorption from the upper wavelength limit of the hydrocarbon up to 4000 or 5000 A, while the halogen complexes have an intense absorption band at about 3000 A. In changing from benzene to mesitylene the maximum of this absorption band in SO_2 complexes varies from 2800 to 3050 A, increasing methylation of the benzene type component having the effect of shifting the band toward the visible. On the other hand, complexes with iodine, which are more stable, have their absorption peaks at 2900 A for benzene complexes and 3300 A for mesitylene complexes. In general, then, the stronger the complex, the further toward the visible is its complex absorption band.

In addition to this absorption band which is characteristic of the complex, we find the absorption spectra of the separate components, although somewhat modified. For instance, the strong absorption band of iodine at 5200 A is found at 5000 A in benzene $-I_2$ complex, and at 4900 A in mesitylene $-I_2$, the degree of shift of the band being apparently a function of the stability of the complex.^{5,6}

Recently a new absorption band has been found in complexes of benzene with iodine and bromine.³⁰ This band is at 2600 A, and is thought to be a ten-fold intensification of the 2600 A benzene transition $A_{lg} - B_{2u}$.

MOLECULAR ORBITAL THEORY OF MOLECULAR COMPLEXES

Having reviewed what is known experimentally about // electron complexes, we will now examine briefly the current theory concerning these complexes and their spectra.

The idea that there is a partial transfer of charge from, say, a benzene molecule B to a complexed bromine molecule A, can be expressed mathematically by saying that the wave function for the ground state N of the complex is a linear combination of a no-bond wave function, $\bigvee_{0}(A, B) = \bigvee_{R} \bigvee_{B}$, and a bonding wave function in which there is a covalent bond between the unpaired electrons in A⁻ and B[†], ie. $\bigvee_{1} =$ $\bigvee_{1} (A^{-} - B^{\dagger})$

Thus $\bigvee_{N} = a \bigvee_{0} + b \bigvee_{1}$ where $a^{2} \gg b^{2}$ (1) Since \bigvee_{N} , \bigvee_{0} and \bigvee_{1} are normalized we have $a^{2} + 2 ab S + b^{2} = 1$ where $S = \int \bigvee_{0}^{*} \bigvee_{1} dT$ Now W_{N} , the energy of the complex is given by $W_{N} = \int \bigvee_{N}^{*} H \bigvee_{N} JT$

where $H_{\rm L}$ is the exact Hamiltonian operator for the complex.

 W_{N} may be calculated using second order perturbation

theory.

From equation 1. we get the secular equation

$$\begin{vmatrix} & & & \\ &$$

For a sufficiently accurate approximation we may let $W_N = W_O$ for all but the first term, since essentially the

difference is small.

Now we have

$$\begin{vmatrix} W_{o} - W_{N} & H_{ol} - SW_{o} \\ H_{g} - SW_{o} & W_{l} - W_{o} \end{vmatrix} = 0$$

or $W_N \simeq W_0 - (\frac{H_{ol} - SW_0}{(W_1 - W_0)}^2)$

 W_{0} , the energy of the no-bend function includes any classical dipole - dipole attractions, as does W_{1} , which includes as well the attraction energy of the covalent bond.

The resonance energy of the ground state is now given by $W_0 - W_N$, this being due to interaction between V_i and V_i . $W_0 - W_N$ will be large if $(H_{ol} - SW_0)^2$ is large, that is, if V_i and V_i overlap strongly, and if $W_1 - W_0$ is fairly small.

If the ground state of a complex is given by equation (1) then there must be an excited state with wave function $\Psi_E = \alpha^* \Psi_i - \beta^* \Psi_i$ with a $\approx a^*$

and b pprox b*

Then by the same method as before

 $W_{E} = W_{1} + \frac{(H_{o1} - SW_{1})^{2}}{(W_{1} - W_{o})^{2}}$

Thus a transition from $W_E \leftarrow W_N$ should exist, and its transition probability could be calculated. Since $a^2 >> b^2$, we see that \bigvee_N has almost pure no-bond character; while \bigvee_E has almost pure ionic character, so that the transition $W_E \leftarrow W_N$ may be considered an intermolecular charge - transfer process; that is, light absorption causes an electron to jump

-10-

from B to A.

This electron transfer band is obviously a property of the complex as a whole, and the absorption spectra of the separate molecules are expected as well, although perhaps slightly modified. It is possible that these intramolecular states may overlap or interfere quantum-mechanically with the charge-transfer excited state, so that it may be difficult to distinguish the original molecular spectrum.

In Fig. 2 may be seen the potential energy curves of the states W_N and W_E for the benzene-iodine complex molecule as a function of R, the distance between the centres of the two complexing molecules,



Fig. 2. Botential energy curves for the states W_N and W_E of the benzene $-I_2^{<}$ complex. I_B vert. is the vertical ionization potential of benzene. E vert. is the vertical electron affinity of iodine.

This, of course, does not say that complex formation does not occur between one component and an excited state of the other, as this very likely happens.

The foregoing treatment, due to Mulliken,⁵⁰ is the one which has been the most successful in explaining the absorption spectra of molecular complexes.⁴⁷ PHENOMENA NOT IMMEDIATELY EXPLAINABLE BY CHARGE TRANSFER,

There have been phenomena observed, however, which suggest that a charge-transfer transition may be to a nonbonding state of the $\hat{1}$ complex.

Kasha has observed a yellow colouration appearing in solutions of \prec -chloronaphthalene and ethyl iodide which he attributes to the formation of a collisional complex, since the yellow colour disappears in rigid glass. Kasha interprets the yellow colouration as being due to an increase in the T \leftarrow S absorption in \prec -chloronaphthalene. This increase in absorption for a forbidden transition is considered to be due to a collisional perturbation which affects the T \leftarrow S transition probability.³⁶

Somewhat similar were the conclusions of Reid concerning hydrocarbon complexes with s-trinitrobenzene. He found that the complexes, in rigid solution, when irradiated in an absorbing region emit a short-lived radiation in the region of the long-lived hydrocarbon triplet emission. This suggested that the absorption was to a repulsive state of the complex, and that the hydrocarbon is left in its first triplet state, the s-trinitro-benzene in its ground @ state. The varying field produced by the decomposition of the complex is assumed to be sufficient to break down the T \rightarrow S selection rule, so that the transition will be allowed and therefore short lived.^{58,59}

-12-

PHENOMENA EXPLAINED BY COMPLEX FORMATION

The formation of molecular complexes makes possible the explanation of a number of phenomena, among which are energy transfer and fluorescence quenching.

Consider first energy transfer: Foster has found instances of energy transfer between various large organic molecules, for instance between tripaflavine and rhodamine B, in fairly concentrated solutions. He has also developed a theory showing that a long-range dipole-dipole interaction should exist between such molecules.

However, working with far more dilute rigid solutions of hydrocarbons, Moodie and Reid have shown that long distance transfer of energy is not possible under these conditions between randomly distributed molecules of different compounds, but that energy transfer requires complex formation. Furthermore, they have found no evidence for complex formation between single pairs of molecules, but only between molecules of one hydrocarbon and microcrystals of another. In such complexes, presumably, the microcrystal would act as the "Lewis base", the hydrocarbon molecule as the acceptor. This phenomen explains why it is so extremely difficult to obtain some hydrocarbon, such as anthracene and chrysene, free from other hydrocarbon contaminants, such as naphthacene.⁴⁸

That fluorescence quenching is often due to molecular complex formation has been found by a number of investigators. ^{33,34} Bowen and co-workers, for instance, have found that substituted benzenes and toluenes, in quenching anthracene fluorescence in solution, either form true complexes with the anthracene or else form loose collisional complexes.^{9,11,12} Complex formation is also indicated as being responsible for quenching of anthracene fluorescence by O_2 and SO_2 in the vapour phase.¹⁵

Whether two molecules will form a collisional complex or a true complex, the latter being characterized by a negative temperature coefficient, is often determined by steric effects, 5^{2} , 6^{0} , as well as by the tendency of the two components to act as Lewis acids or bases. For instance quenching of rubrene fluorescence by nitrobenzene arises from true complex formation, while quenching by m-dinitroand s-trinitrobenzene is due to collisional quenching. This seems to be the opposite of what would be expected from previous considerations. However, if complex formation requires that the ring systems be parallel, then it may be imagined that the nitro groups on the m-dinitro- and s-trinitrobenzenes would interfere with the phenyl groups at right angles to the plane of the rubrene molecule.¹³

Also from Bowen comes the information that in crystals of anthracene, fluorescence is quenched by impurities of acridine or phenazine.¹⁶ This is probably due to the same type of energy transfer as occurs between anthracene and naphthacene impurity,¹⁴ except that here, instead of anthracene excitation energy being emitted by

-14-

the impurity, as is the case with naphthacene, the energy when transferred to the heterocyclics, is lost by vibrational deactivation before it can be emitted.

More recently, however, Bowen, among others, 27,67 , has supported the idea of quenching being due to long-range energy transfer and long-range \mathcal{M} electron interaction, in certain cases, rather than complex formation.¹⁰

REASON FOR THE PRESENT INVESTIGATION

The present investigation of complex formation with heterocyclic compounds was undertaken for several reasons, the most important of which are, first, heterocyclics are known to form stable complexes with picric acid and trinitrobenzene, which should have interesting spectroscopic properties; and second, heterocyclics might reasonably be expected to form more stable complexes with hydrocarbons than do ther hydrocarbons, and might thus be detected in solution without microcrystals of one component. This seems even more possible since Terenin and Karyakin have detected energy transfer between naphthalene and acridine in the vapour phase.^{65,66}.

A REVIEW OF THE ELECTRONIC PROPERTIES OF HETEROCYCLICS

It will be well to review what is known of the energy levels and other electronic properties of heterocyclics, as this will show that for heterocyclics, unlike hydrocarbons, even fairly accurate determination of energy levels is yet impossible. As was seen in the discussion of the benzene-iodine complex, it is necessary to be able to determine the energy of a given molecular orbital as well as its symmetry in order to know whether or not it will enter into stable complex formation.

The energy levels of any cata-condensed hydrocarbon may be calculated fairly accurately as is shown by the good agreement obtained between experimental and calculated resonance energies and allowed transition energies.^{1,37,26, $4^{2,54-56}$, Thus, if the "acid" molecule may also be treated theoretically with some accuracy, then it should be possible to calculate at least relative interaction energies for hydrocarbon complexes, provided simplifying assumptions may be made about the symmetry of the complex, which of course, is not always the case.}

In contrast with aromatic hydrocarbons, heterocyclics have proven rather difficult to deal with theoretically. The main reason for this is that the diagonal or coulomb terms in the secular equation (written in matrix form) which correspond to the attraction of a nucleus for its own electron, must vary in heterocyclics; the only way these variations in coulomb integral can be taken into account is by introducing empirical parameters. This method gives quite satisfactory results for electron densities and bond orders, but very poor results for the resonance energy.^{40,43} A more convenient method has been developed of treating an aza-substitution as a perturbation

-16-

of the parent hydrocarbon system; this method, however, gives no information concerning energy levels. 20-23,41.

A semi-empirical method has been devised by Dewar for obtaining the energies of molecular orbitals of pyrroletype compounds.²⁴ In pyrrole the C-N bonds have lower bond orders than the C-C bonds, and the nitrogen has more than its share of the six electrons, both facts being due to the higher electronegativity of nitrogen. However, this charge distribution should also exist in the hypothetical $\langle \chi \rangle$, where the C-X exchange integral is much less than that of C-C, but the coulomb integral for X is equal to that for C. This method gives fairly good values of the resonance energy in pyrrole-type compounds, but, of course, cannot be extended indescriminately to other types of heterocyclics.

TRANSITIONS FOUND IN HETEROCYCLICS,

We will now consider the transitions which are expected and found experimentally in most heterocyclics.³⁵ It will be convenient to consider the following diagram.



Fig.3. G is the ground state, S_1 and S_2 the first and second excited singlet states, and T_1 and T_2 are the first and second triplet states.

 T_1 and T_2 corresponding the unpairing of the excited electron

-17-

and the one left behind in the now half empty orbital. The solid vertical lines indicate optical transitions, while the dotted ones indicate radiationless transitions. The transition $S \leftarrow G$ corresponds to the excitation of an electron from the filled T molecular orbital having the highest potential energy, to the lowest antibonding orbital having the correct symmetry to fulfil the requirement that the integral for the transition probability, $\int \Psi_{c} \succ \Psi_{S} dT$, where X stands for any distance coordinate, shall remain invariant under any symmetry operation of the molecule.

The optical transition $T_1 \rightarrow G$, and the radiationless transitions $S_1 \rightarrow T_1$, etc, are forbidden, since they involve a change in multiplicity. However, these transitions may be made partially allowed by spin-orbit coupling, a phenomenon in which, instead of the ordinary L-S coupling that mainly occurs with small atoms, there is also a small amount of j - j coupling.^{44,45} This results in a slight mixing of certain of the singlet levels with the triplet level in question, making transitions between it and singlet levels partially allowed. Since the amount of spin orbit coupling in a molecule is a function of the square of the charge on the nucleus of the heaviest atom present, heterocyclics should show slightly more allowed triplets than hydrocarbons.

Another transition which is expected to some extent in heterocyclics, is the so-called $n \rightarrow T$ transition, in which one of the non-bonding electrons on the nitrogen is excited up to the $/\!/$ system. This transition is forbidden by symmetry, but has been observed weakly in absorption in pyridine and pyrazine as well as other compounds.^{29,57,} This transition is recognizable by the fact that it shows a blue shift in increasingly polar solvents,⁴⁶, and disappears completely upon salt formation, with, say, sulphuric acid.

For any transitions which are semi-forbidden to show up in emission, it is necessary to use low temperatures and rigid glass solvents, since if collisions are possible, deactivation of the metastable state will occur by collision before radiation is possible.



Apparatus Used in This Investigation

-20-

Experimental Methods and Results.

APPARATUS

A photograph of the apparatus used in this investigation will be seen on the preceeding page. The apparatus for studying emission spectra consisted of a General Electric A. H. 6 high pressure mercury arc with suitable filters as a light source, a Hilger E2 spectograph, and Hilger scanning unit and photographic recorder.

-21-

Absorption spectra were obtained in some instances using the spectrograph with a Beckman hydrogen lamp, in which case the spectra were photographed on plates. A Beckman spectro-photometer was also employed in obtaining certain of the absorption spectra. Measurements of relative intensities were made using a Hilger non-recording photo-electric microphotometer.

A simple phosphoroscope was also used to some extent. This consisted of a metal can with a slit in the side which was rotated by means of a small motor.

PROCEDURE

Solutions of the heterocyclics and their polynitro complexes were made using solvents which will form a rigid glass at -180° C. the temperature of liquid nitrogen. Test tubes of these solutions were frozen down in a transparent quartz or Vycor dewar vessel, and irradiated with 3100A, 3650 A, or 4358 A light from mercury arc. The emissions were recorded with the scanning unit in the region from approximately 3500 to 5500 A. In the region from 5000A up, Eastman Kodak IIF 3 plates were used.

The required mercury line was isolated using the following filters: Corning filter 754 with nickel sulphate solution for 3100A, filter number 737 for 3600A and filter number 5.74 for 4358A.

For absorption spectra below 3000A, the problem of suitable holders for the rigid solutions arose, since pyrex does not transmit appreciably below this wave length. A reasonably satisfactory solution to the problem was found in the "popsicle" technique. For this technique a small brass vessel about 10 cm. deep and 1.5 x 1.5 cm. across is made and fitted with a long handle. The liquid to be frozen is poured into this vessel, and the whole thing placed in liquid nitrogen. When it is hard, a thin rod is thrust well into the frozen solvent. When the rod is solidly frozen in, the whole vessel is placed in cold water, and the rod is used to pull out the block of solvent, the sides of which have now melted slightly. This "popsicle" may then be transfered to the quartz dewar, and has the advantage of having flat surfaces, a very desirable feature in obtaining absorption spectra.

The absorption spectra were recorded on Eastman Kodak IN plates, intensity comparisons being made with pure solvent popsicles at varying exposure times.

The absorption spectra of dry solids were obtained

-22-

with the Beckman spectro-photometer by making a solution of the compound in ether and then evaporating off the ether in a quartz Beckman cell. In the case of pure heterocyclic compounds an empty cell was used as a blank, while for the polynitro compound complexes, the blank used was a cell with a thin film of the polynitro compound concerned. This technique had certain disadvantages; for instance, in order to obtain accurate readings on the Beckman, the refractive index of the sample and of the blank should be the same; furthermore, the amount of polynitro compound in the film on the blank cell could never be made exactly equal to the amount in the film containing the complex. In spite of these facts, however, the readings obtained were closely reproducible with regard to wave length, and to a lesser extent with regard to relative intensities of the main absorption bands.

The glass used for most of this work consisted of twelve parts of ethyl ether, five parts of isopropyl ether, and three parts of n-butyl ether with two parts of isopentane added to prevent the glass from cracking readily. However, the above mixture, although ideal as a solvent for heterocyclic compounds, tended to crack upon direct contact with liquid nitrogen. Thus for the "popsicle" technique it was necessary to use E. P. A., a mixture of five parts of isopentane, five parts of ethyl ether and two parts of ethanol. This solvent was also used to find the effect of a more polar solvent on the phenomena observed.

-23-

Purification of the chemicals used was an important preliminary to this investigation, although the materials used were all reagent grade to begin with. The best way to purify the heterocyclic compounds used was found to be by chromatography through columns of alumina, employing low boiling petroleum ether as solvent. The polynitro compounds were purified by repeated recrystallization, the s-trinitrobenzene and m- and p-dinitrobenzenes from ether, and the dinitrocresols from ethanols.

The solvents used had to be both pure and free from water. The isopentane was run through a column containing a layer of silica gel and a layer of alumina, and then distilled. The ethyl ether used was dried with sodium and distilled. The isopropyl and n-butyl ethers were found to be dry, and were just distilled. One hundred percent ethanol was distilled. In this way all the solvents, when frozen down to -180° C., and irradiated with 3100A showed no emission, which indicated a complete lack of large unsaturated impurities.

RESULTS

The polynitrobenzene complexes examined spectroscopically during this investigation fall into two categories: those containing 2,4-dinitro o=cresol or 2,6-dinitro p-cresol, and those containing one of s-trinitrobenzene, p-dinitrobenzene or m-dinitrobenzene.

Complexes of the first type have some salt-like character, being reasonably soluble in water, a fact which.

-24-

indicates that they are, to some extent at least, of the form RNH[†] $OC_6H_3(CH_3)(NO_2)_2^-$, especially with fairly strong bases such as the quinoline compounds. These complexes dissolved in ether show a large increase of colour intensity upon cooling to liquid nitrogen temperature.

On the other hand, complexes with the di- and trinitrobenzenes behave as non-ionic dispersion force complexes as would be expected; they are very insoluble in water. Their absorption intensities indicate a large negative temperature coefficient.

A complex formation between a heterocyclic compound and a nitro compound could usually be recognized at once by the appearance of colour, generally yellow, although in very dilute solutions this colour would not appear until the complex is cooled down considerably.

Of the heterocyclic compounds studied, only acridine and the dibenzacridines absorb as high as 3600 A. The other heterocyclics all have their longest wave length absorption band at 3100 A or a bit lower. The nitro complexes, on the other hand, absorb up into the blue. The emission spectra of the complexes, other than the acridine complexes, were examined with irradiation of 3100 A. and 3650 A.

In investigating the complex emissions using 3100A excitation, varying amounts of the complexing nitro compound were used with constant amounts of heterocyclic

-25-

compound. In many cases in which complex formation occurred, complete quenching of the heterocyclic fluorescence took place upon addition of the non fluorescing nitro compound. This was especially the case with the carbazok-s-trinitrobenzene complex.

However, in other instances, quenching took place more slowly as the amount of nitro compound in solution was increased; furthermore, interesting changes in the emitted radiation could be observed. Consider, for instance, the benzo -(f)- quinoline complex formed with 2,6-dinitro p-cresol solutions to which have been added equal molar quantities of both components (approximately 1 x 10^{-3} mols/1.) still show a long-lived emission in the region of the triplet emission of the benzo (f) quinoline at 4400 to 5300 A. , but there is little band structure remaining. The emission in the region of the 4100 A. triplet band is lost by reabsorption; also the singlet emission of the heterocyclic completely disappears when there is any dinitro-cresol complex present. A phosphoroscope determination of the emission of this solution was made, so that the long-lived component of the radiation could be isolated, and it was found that the structurless emission in between the two long-lived phosphorescence bands is short-lived. (Fig.4. (a) - (e).)

However, it was found possible to add enough dinitrcresol to the benzo (f) quinoline solution to entirely quench the fluorescence of the heterocyclic compound, and in this case there is no sign of any short-lived emission ether.

-26-

The addition of s-trinitrobenzene or m- or p-dinitrobenzene often resulted in partial or complete quenching of a heterocyclic emission, although a loss of structure of the triplet emission was not apparent. The triplet band nearest the blue usually disappears when there is nitro complex present, as does the singlet emission.

Indole, however, was an exception. Its faint shortlived triplet bands in the yellow green were enhanced slightly and made short-lived by complex formation with p-dinitrobenzene.

A summary of the results obtained using 3100 A excitation will be found in Table 1.

Now emission spectra obtained with 3650 A as the exciting light will be considered. Acridine absorbs at this wave length, but not much at 3100 A. The acridine-s-trinitrobenzene complex irradiated with 3600 A exhibits short-lived emission in the acridine triplet region, as has been reported elsewhere.⁵⁸

Now of the complexes of the other heterocyclics, many emit a fairly intense, short-lived radiation in the region of the triplet bands of the heterocyclic, when irradiated with 3600 A light. (Figs. 5, 6, 7). The results obtained for the various complexes are tabulated in Table 11.

It is most important to note that a solution of a heterocyclic compound, such as benzo(f)quinoline with enough nitro compound added to completely quench all emission with 3100 A irradiation, will emit strongly in the heterocyclic

-27-

triplet region when irradiated with 3600 A light.

The above results may be obtained both in ether glass and in the more polar E.P.A.

The emission spectra of the dry solids of most of the foregoing complexes were investigated. In all cases in which a complex in solution showed an enhanced triplet, the dry solid did also, when irradiated with light of the same wave length. This emission of the dry solid was usually shifted a bit to the red of the triplet emission of the heterocyclic. However, there were two cases in which irradiation of the dry solid complex with 3100 A produced the same shortlived emission as did 3600 A light. This occurred in spite of the fact that the complex in solution did not show a shortlived triplet with 3100 A irradiation. For example, this occurred with benzo(f)quinoline, -2,4-dinitro o-cresol complex, and xanthene-trinitrobenzene complex. It should be noted that other complexes in the dry solid state, such as the dibenzofuran-s-trinitrobenzene complex, do not emit appreciably with 3100 A irradiation, but do show an enhanced triplet with 3600 A irradiation.

The s-trinitrobenzene complexes of 1, 2, 5, 6- and 1, 2, 7, 8-dibenzacridine were examined. Using 4358 and 3600 A exciting light, it was possible to see visually that the reddish yellow triplets were enhanced and short-lived in the complex, although the free heterocyclic triplet lifetime, when irradiated with 3600 A is quite long-lived. (Fig. 8). It is interesting to note that the T-N-B complex of the

-28-

former compound is pale yellow, while that of the latter is purple. The dry solids of both complexes show the same reddish yellow emissions as the solutions, although not so bright. These complexes were rather difficult to study in solution, because they are so very insoluble in ether.

The absorption spectra of the complexes trinitrobenzene-xanthene and 2,4-dinitro o-cresol-benzene(f)quinoline were studied, both in solution and as dry solids, and compared with the absorption of the pure heterocyclic compounds.

In both cases it was found that the $/\!/$ absorption of the heterocyclic was retained at the same wavelength in the complex, a continuous absorption region extending from the end of the long wave limit of heterocyclic absorption up to 4500-5000 A. (Figs. 9, 10). It was assumed that the nitro compound absorption remained pretty well unchanged as a decreasing absorption from about 2600 A to 3000 A, so that the blank of nitro compound could be used. The absorption spectrum of benzo(f)quinolinium hydrochloride was also obtained, (Fig.10), and it will be seen that there is an extra absorption peak at 3650 A which appears neither in the free base, nor in the complex.³²

In an effort to determine whether any of the longlived emission in benzo(f)quinoline is n-,//, the emission was observed using the increasingly polar series of solvents, a. Four parts methyl cyclohexane plus one part isopentane; b. Ether mixture (see page 23); c. E. P. A.; d. eight parts ethanol, one part methanol, one part isopropanol. How-

-29-

ever, no detectable shift was observed.

It was thought that AlCl₃, being a good Lewis acid, might form molecular complexes with heterocyclics. However, its effect was observed with quinoline and carbazole, and there was no sign of *f*-complex formation. This is not surprising since AlCl₃ does not form *f*-complexes with hydrocarbons.¹⁹

Since trimesic acid has an electron deficient ring, it was thought that it might form complexes with heterocyclics, and indeed, it does form a yellow complex with acridine, although not visibly with any of the other heterocyclics tested. However, neither acridine-trimesic acid solutions nor those with any other heterocyclic compounds showed any emissions that were not identical with the heterocyclic emissions.

The heterocyclic compounds were all examined for complex formation with naphthacene solution and suspension. But there was no sign of complexes with naphthacene molecules, although there were three instances of complexes between heterocyclic and naphthacene microcrystal. These include dibenzofuran and benzofuran, both of which show a new band at 5250, indicating energy transfer to naphthacene suspension,⁴⁸ and dibenzothiophene which shows quenching of emission in contact with naphthacene suspension.

-30-

Table 1.

Effect on heterocyclic triplet emission of complex formation, in rigid solution, irradiating with 3100 A.

	2,6-dinitro- p-cresol	2,4-dinitro- o-cresol	s-trinitro- benzene	p-din itro- benzene
Indole	quenching		quenching	enhanced trip- let,4600- 6 000A
Carbazole	no apparent complex.	no apparent compl ex.	quenching(also for dry solids).	
Benzofuran	some quenching.	some quenching.	some quenching.	
Dibenzofuran	quenching (also dry solid)	quenching (also dr y s olids)	quenching (als0 dry solids)	quenching (also dry solids)
Dibenzothiophene	quenching	quenching	some quenching, some loss of band structure.	quenching
Xanthene	no apparent complex.	no apparent complex.	not completely complexed, some quenching, some enhanced triplet (more enhanced triplet with dry solid).	
Quinoline (also quinaldene)	loss of structur ing.	e and quench-		
Benzo(f)quinoline (also_3-methyl benzo(f)quinoline	loss of structur ing.	e and quench-	quenching.	May not complex.

.

Table 11. Emission with exciting light of 3600 A. (in rigid solution)

.

· · · · · · · · · · · · · · · · · · ·		·	~	
· · · · · · · · · · · · · · · · · · ·	2,6-dinitro- p-cresol	2,4-dinitro- o-cresol	s-trinitro- benzene	p-dinitro- benzene
Indole		faint short- lived, yellow.	faint short- lived, 4 6 00 - 6000A	strong short lived, 4600 - 6000 A.
Carbazole	no emission.	no emission.	no emission.	no emission.
Benzofuran	short-lived emiss	sion in triplet re	egion).	
Diobenzofuran	· · ·	short-lived emission in triplet region.	ehhanced short- lived emission triplet region.	in
Dibenzothiophene	short-lived emis:	sion in triplet r	egion	
Xanthe ne		quenching.	short-lived emission in triplet region.	
Quinoline (also quinaldene)	strong short- lived emission in triplet region.	1	faint emission in triplet regi	Faint emission in on. triplet region.
Benzo(f)quinoline (also 3-mehhyl benzo(f)quinoline)	strong short-live triplet region.	ed emission in	quenching.	

ယ်လို



Fig. 4. Emission spectrum of benzo(f)quinoline, and of the benzo(f)quinoline-2,6-dinitro p-cresol complex, in solution in ethers, irradiated with 3100 A; All the emission spectra shown here are long-lived. a. benzo(f)quinoline; b. benzo(f)quinoline, 2,4dinitro p-cresol, relative molar quantities 2:1; c. same as b; proportion 1:1; d. as b, except proportion 1:2; e. Same as for c, using phosphorscope.



Fig. 5. Emission spectrum of dibenzofuran, and of its complex with s-trinitmobenzene.

a.

dibenzofuran irradiated with 3100 A, long-lived. dibenzofuran-s-trinitrobenzene complex irradiated with 3600 A, short-lived. ъ.

-34-



Fig. 6. Emission spectrum of xanthene, and of its complex with s-trinitrobenzene.

a. xanthene irradiated with 3100 A, long-lived component.
b. Solid curve, xanthene s-trinitrobenzene complex irradiated with 3600 A, short-lived.
Dotted curve - complex dry solid with 3600 A light.

-35-



Fig. 7. Emission spectrum of benzo(f)quinoline, and of its complex with 2,4-dinitro o-cresol. a. benzo(f)quinoline irradiated by 3100 A, long-lived

portion.

benzo(f)cuinoline - 2,4-dinitro o-cresol complex irradiated with 3600 Å, shbrt-lived. Dry solid complex irradiated with 3600 Å. b.

с.



Fig. 8. Emission spectrum of 1, 2, 7, 8- dibenzacridine and of its s-trinitrobenzene complex. a. 1, 2, 7, 8-dibenzacridine alone, long-lived emission.

b. s-trinitrobenzene complex in rigid ether solution, short-lived.

ن الجامع



a. xanthene;

b. xanthene-s-trinitrobenzene complex





DISCUSSION

First we will consider the phenomena which take place with benzo(f)quinoline-dinitro-cresol complexes. As was mentioned earlier, a solution may be made so concentrated in nitro compound that it is completely quenched with 3100 A radiation, and yet show strong fluorescence in the triplet region of the benzo(f)quinoline when irradiated with 3600 A light. We have seen from the absorption spectra diagram (Fig. 10) that the complex absorbs at 3100 A even more strongly than it does at 3600 A. The occurrence of strong emission upon irradiation with 3600 A and not 3100 A must mean that in the two cases absorption is to different excited states. Now if the absorption region which lies at longer wave lengths than the original heterocyclic \mathbb{Z} absorption is a charge-transfer transition directly to a non-bonding state of the complex, such that the complex dissociates leaving the heterocyclic compound in its triplet state, then one would expect that irradiating the complex with a slightly higher energy radiation would produce the same results. Thus it seems likely that the transition excited with 3100 A is to a bonding state of the complex. That is, the state $\Psi_{comp} = \Psi_B^* \Psi_A +$ Ψ (B⁺⁻ A⁻) can be a bonding state of the complex as long as the symmetries of the orbitals are correct, where V_R^{\star} represents the first excited singlet of the heterocyclic compound belonging, to some extent, to the whole complex. From here the excitation energy is lost by vibrational deactivation and radia-

-39a-

ationless crossings to the ground state. One would not expect the complex as a whole to emit this energy in an optical transition in view of the presence of vibrating nitro groups and other factors.

It seems likely that the charge-transfer transition excited by 3600 A light is to a bonding state of the complex also, namely to the state E described on page 11. However, this state E is at very closely the same energy as the heterocyclic triplet level, and the possibility of a radiationless crossing to the heterocyclic triplet level is suggested. If such a transition state should occur, then the complex would be in a repulsive state and would dissociate. The changing field produced by dissociation could be assumed to make the transition to the ground state allowed, as was mentioned on page 12.

There are two apparently serious objections to the idea of such a radiationless transition: these being that the transition would be both multiplicity and Frank-Condon forbidden. Dealing with the multiplicity selection rule first, it seems that the objection is not too serious since spin-orbit coupling will occur, to produce mixing into the triplet state of some singlet character and vice versa. This effect will be quite small since the N and O atoms present have quite small Z values. However, spin-orbit coupling is sufficient in other compounds such as hydrocarbons to produce a radiationless transition from excited singlet to triplet so that

-40-

this selection rule will nortainly not be unsuperable here.

Turning now to the objection that the inter-combination is Frank-Condon forbidden, it will be convenient to consider the complex as two potential wells separated by a fairly high barrier. This can be looked upon as an extension of the free electron method, 4,18,61, similar to the extension made by Shuler for the case of a two dimensional T electron complex.⁶²



Wave functions will look more complicated for actual T complex bonding orbitals, since their electronic quantum numbers will be high; however, the tunnel effect will occur even more for higher orbitals.

Fig.ll. Two different potential wells separated by fairly high barrier.

The barrier height is proportional to $E_A - I_B$, E_A being the electron affinity of the Lewis acid, and I_B the ionization potential of the Lewis base. Now if we take 1 as the perturbed ground state level of the heterocyclic, then 1 to 2 may be considered the charge-transfer transition; while 1 to 3 will be the slightly modified transition to the first excited singlet of the heterocyclic compound. Now suppose that the triplet state corresponding to 3 is below 2 in energy. The statement that the transition 2 to 3 (triplet) is Frank-Condon forbidden means that an electron cannot make the transition without a

С

change in its position. At first one would tend to think of the transition from a charge-transfer state to the heterocyclic triplet as a movement of the electron across the complex to some extent. However, observing Fig. 11, one can see that the electron, even in its excited state 2, has a considerable possibility of being on the heterocyclic molecule. Thus it should be possible for a 2 to 3(triplet) transition to take place after all, on these considerations at least.

If spin-orbit coupling in the complex is responsible for the multiplicity selection rule being broken down somewhat, then there arises the question of why the complex, when in the excited but modified heterocyclic singlet state, does not show some radiationless transition to the triplet for the same reason of enhanced spin-orbit coupling. However, if the effect of triplet mixing into singlet states is to be considered as well as the reverse, then it must be the case that the level 2 will be more affected by spin-orbit coupling than level 3 (singlet). Once an orbital has become perturbed by spin-orbit coupling then its effect would have to be much the same over the whole complex for that orbital, since an electron cannot be expected to change its degree of singlet or triplet character according to its position in an orbital. However, the nitro groups in the "acid" part of the complex are responsible for the strongest spin-orbit coupling, and surely the orbital with the highest probability density on the nitro compound will be the most affected by spin-orbit coupling.

-42-

In addition the charge-transfer excited electron would not have the same probability of deactivation to ground as would the first excited singlet of the heterocyclic, as it involves very different transitions back to ground, so that it is not essential that radiationless transitions occur to the same degree for both levels, even if the spin-orbit coupling argument did not exist.

The energy of the charge-transfer transition can be expected to increase with decreasing strength of complex This will provide an explanation of why the dry formation. solids of certain complexes, eg., dinitrocresol and benzo(f) quinoline, emitted a short-lived triplet radiation with 3100 A light when the solution did not. The forces between molecules of a solid are not enough to change the wave length of absorption of an ordinary molecule, although they are responsible often for small maxima beyond the long-wave length end of the absorption of the molecule. However, in the case of weak complexes, the forces between molecules of complex will be of almost the same order as the forces between the components of the complex, and a shift of the charge-transfer spectrum to higher energies is expected. Another way of looking at this is that the attractive forces between complex molecules in a crystal provide: a lowering of potential energy for the ground This will result in a blue shift of any transition to a state. state differing a great deal from the ground state.

It seems likely that the benzo(f)quinoline forms a slightly fluorescing complex with trinitrobenzene because of

-43-

the increased strength of the complex, so that the excited charge-transfer state will not be much above the triplet state of the heterocyclic, and the cross-over will occur only to a small extent. The tendency of the dinitrocresols to form true salts in polar solvents will not increase the tendency for // complex formation, rather the added hydroxy group will activate the ring and decrease the tendency for the ring system to act as a Lewis acid.

The fact that the complexes of benzo(f)quinolinedinitrocresol showed short-lived emission between the triplet bands of the heterocyclic with 3100 A irradiation must be due to the reabsorption by the complex of strong heterocyclic singlet emission.

The fact that indole shows an enhanced triplet upon irradiating with 3100 A light is probably due to the fact that it forms a weaker complex than many of the other heterocyclics. Although the carbon atoms on the pyrrole ring have a higher charge density than they would in, say, benzene, yet the // orbitals are not as free to yield electron density in further bond formation because of the competition for electrons which comes from the presence of electronegative nitrogen.

These considerations will result in a slight lessening of aromatic character for the indole ring system, and a lowering of polarizability. This lessening of aromaticity resulting from not having completely delocalized M orbitals will result in a lowering of the energies of the top bonding orbitals, so that a charge-transfer transition will be of

-44-

higher energy than for a more fully aromatic ring system.

The same consideration will be true, though to a lesser extent, for carbazole. However, the reason carbazole complexes do not fluoresce with irradiation of either 3100 A or 3600 A is probably that the carbazole triplet levels are at too high energies.⁵⁸

Xanthene, too, should form weaker complexes and its complexes have a higher energy charge-transfer transition because of the lessening of aromaticity resulting because the conjugation of the ring system is broken to some extent.

The quinoline and acridine complexes, on the other hand, should be stronger, since there is no question of lessening of aromatic character and resulting loss of polarizability.

The fact that trimesic acid did not result in complex formation other than with acridine is not surprising, since it will be a much weaker Lewis acid than is a polynitrobenzene compound. Even if it did form complexes, the resulting absorption region would not be expected to be in the same region as for the nitro complexes, so that cross-over to the heterocyclic triplet would not necessarily be expected.

It is also not too surprising that complex formation was not observed between heterocyclics and hydrocarbon molecules, since there is not enough difference between the electron densities on the two rings. In the case of hydrocarbon crystals, however, the matter is quite different, since electrons are known to move with a certain degree of freedom throughout the whole crystal, and the electron density at the

-45-

surface of the crystal could be expected to be high, so that the microcrystal could act readily as a Lewis base, in the presence of heterocyclic molecules, which will be capable of accepting some of this sumplus electron density, especially since in benzo and dibenzofuran, the compounds for which transfer to hydrocarbon crystals occurred, the furan ring system has not got the complete six electrons it needs for aromatic character in a state delocalized from the oxygen atom.

Further work on the problem of heterocyclic complex formation with nitro compounds should include the following investigations:

- 1). More detailed examination of the absorption spectra of the complexes at low temperatures with equipment giving higher resolution that it was possible to obtain here.
- 2). Investigation of exact quantum yields of these complexes, with a view to finding how much energy is lost by vibrational deactivation and other means.
- 3). Polarization studies coupled with theoretical investigations of the expected polarizations of the various theoretically expected transitions.

-46-

- BIBLIOGRAPHY -
S.L.Altman, Proc. Phys. Soc. (London) <u>A63</u> , 1234(1952).
L.J.Andrews and R.M.Keefer, J.Am. Chem.Soc. 73, 462(1951).
L.J.Andrews and R.M.Keefer, J.Am.Chem.Soc. 73, 4169(1951).
N.S.Bayliss, Quart. Rev. <u>6</u> , No.4, 319(1952).
H.A.Benesi and J.H.Hildebrand, J.Am.Chem.Soc.70, 2832(1948).
H.A.Benesi and J.H.Hildebrand, J.Am.Chem.Soc. <u>71</u> ,2703(1949).
G.Berthier and B.Pullman, Compt.Rendu. 231, 774(1950).
N.W.Blake, H.Winston and J.A.Patterson, J.Am.Chem.Soc. 73, 4437(1951).
E.J.Bowen, Quart.Rev.Chem.Soc.(London) 1, 1(1947).
E.J.Bowen, Symposia of the Society for Exp'tal. Biology, <u>5,</u> (1951).
E.J.Bowen, A.W.Barns and P.Holliday, Trans. Faraday Soc. 43, 27(1947).
E.J.Bowen and E.Coates, J.Chem. Soc. 105(1947).
E.J.Bowen and E.Coates, J.Chem.Soc. 131(1947).
E.J.Bowen and P.D.Lawley, Nature, <u>164</u> , 572(1949).

- 15. E.J.Bowen and W.S.Metcalf, Proc.Roy.Soc.(London) A206, 437(1951).
- 16. E.J.Bowen, E.Mikiewicz and F.W.Smith, Proc.Roy.Soc. (London) <u>A62</u>, 26(1949).
- 17. E.Boyland, Cancer Research, <u>12</u>, 77(1952).
- 18. L.G.S.Brooker and W.T.Simpson, Ann.Rev.Phys.Chem.2,121(1951)
- 19. H.C.Brown, H. Pearsall and L.P.Eddy, J.Am. Chem. Soc. <u>72</u>, 5347(1950).
- 20. C.A.Coulson and H.C.Longuet-Higgins, Proc.Roy.Soc.(London) A191, 39(1947).

1.

2.

3.

4.

5.

6.

7.

8.

9.

10.

11.

12.

13.

14.

- 21. C.A.Coulson and H.C.Longuet-Higgins, Proc.Roy.Soc.(London) A192, (1947). 16.
- 22. C.A.Coulson and H.C.Longuet-Higgins, Proc.Roy.Soc.(London) <u>A193</u>,447(1948).
- 23. C.A.Coulson and H.C.Longuet-Higgins, Proc.Roy.Soc.(London) <u>A193</u>2 456(1948).
- 24. M.J.S.Dewar, The Electronic Theory of Organic Chemistry (Oxford, at the Clarendon Press, England, 1949).
- 25. M.J.S.Dewar, Trans Faraday Soc. <u>42</u>, 764(1946).
- 26. K.Fukui, T.Yonezawa and H.Shingu, J.Chem.Phys.<u>20</u>, 722(1952).
- 27. M.D.Galanin, Izvest. Akad.Nauk., S.S.S.R., Ser. Viz. <u>15</u>, 5-43-9-(1951).C.A. <u>46</u>, 8971⁶(1952).
- 28. E.H.Gilmore, G.E.Gibson and D.S.McLure, J.Chem.Phys. <u>20</u>, 829(1952).
- 29. F.Halverson and R.C.Hirt, J.Chem.Phys. <u>19</u>, 711(1952).
- 30. J.S.Ham, J.R.Platt and H.McConnell, J.Chem.Phys. <u>19</u>, 1301 (1951).
- 31. D.L.Hammick and R.B.M.Yule, J.Chem.Soc. 1539(1940).
- 32. J.M.Hearn, R.A.Morton and J.C.E.Simpson, J.Chem.Soc. 3318(1951).
- 33. A.V.Karyakin, Izvest.Adad.Nauk. S.S.S.R., Ser. Fiz. <u>15</u>, 556(1951). C.A. <u>46</u>, 8971^h(1952).
- 34. A.V.Karyakin, Zhur² Fiz. Khim. <u>26</u>, 96(1952). C.A. <u>46</u>, 9983^e(1952). Soc.
- 35. M.Kasha, Disc. Faraday/on Spectroscopy and Molecular Structure, 14(1950).
- 36. M.Kasha, J. Chem. Phys. <u>20</u>, 71(1952).
- 37. H.B.Klevens and J.R.Platt, J.Chem.Phys. <u>17</u>, 470(1949).
- 38. J.Landauer and H.McConnell, J.Am.Chem.Soc. 74, 1221(1952).
- 39. G.H.Locket, J. Chem. Soc. 1501(1932).
- 40. H.C.Longuet-Higgins and C.A.Coulson, Trans. Faraday Soc. <u>43</u>, 80(1947).

-48-

41. H.C.Longuet-Higgins and C.A.Coulson, J.Chem.Soc.971(1949). 42. H.C.Longuet-Higgins and G.W.Wheland, Ann.Rev.Phys.Chem. Vol. 1, (1950)133. 43. P.Lowdin, J. Chem. Phys. 19, 1323(1951). 44. D.S.McClure, J. Chem. Phys. <u>17, 905(1949).</u> 45. D.S.McClure, J. Chem. Phys. <u>20</u>, 682(1952). 46. H.McConnell, J.Chem. Phys. <u>20</u>, 701(1952). 47. H.McConnell, J.S.Ham and J.R.Platt, J.Chem.Phys.<u>21</u>,66(1953). 48. M.M.Moodie and C.Reid, J.Chem. Phys. <u>20</u>, 1510(1952). 49. R.S.Mullikin, J. Am. Chem. Soc. 72, 600(1950). 50. R.S.Mullikin, J. Am. Chem. Soc. 74, 811(1952). 51. B.S.Neporent, Izvest. Akad. Nauk. S.S.S.R., Ser. Fiz. C.A. <u>46</u>, 8970N(1952). <u>15</u>, 533(1951). 52. M.Orchin, J. Org. Chem. <u>16</u>, 1165(1951). 53. P.Pfeiffer; Ann. <u>412,</u> 291(1916). 54. J.R.Platt, J. Chem. Phys. <u>17</u>, 484(1949). 55. J.R.Platt, J. Chem. Phys. <u>18</u>, 1168(1950). 56. J.R. Platt, J. Chem. Phys. 19, 101(1951).57. C.Reid, J. Chem. Phys. <u>18</u>, 1673(1950). 58. C. Reid, J. Chem. Phys. <u>20, 1212(1952).</u> 59. C. Reid, J. Chem. Phys. <u>20</u>, 1214(1952). 60. J.C.Rowell and V.K.LaMer, J. Am.Chem.Soc. <u>73</u>,1630(1951). 61. K.Rudenberg and R.G.Parr, J.Chem.Phys. <u>19, 1268(1951).</u> 62. K.E.Shuler, J. Chem. Phys. <u>20</u>, 1865(1952). 63. H.Shull and F.O.Ellison, J.Chem.Phys. <u>19</u>, 1610(1951). 64. H.Sponer and E.Teller, Rev. Mod. Phys. 13, 99(1941).

-

- 65. A.N.Terenin and V.L.Ermolaev, Doklady Akad. Nauk. S.S.S.R., <u>85</u>, 547(1952). C.A. <u>46</u>, 9994b(1952).
- 66. A.N.Terenin and A.V.Karyakin, Doklady Akad. Nauk. S.S.S.R., <u>58</u>, 425(1947). C.A.<u>46</u>, 4373a(1952).
- 67. A.N.Ternin and A.V.Karyakin, Izvest. Adad. Nauk. S.S.S.R., Ser. Fiz. <u>15</u>, 550(1951). C.A.<u>46</u>, 8981e(1951).
- 68. J.Weiss, J.Chem. Soc. 245(1942).
- 69. R.B.Woodward, J.Am. Chem. Soc. <u>64</u>, 3058(1942).

- - - - -

Appendix.

Syntheses of heterocyclics undertaken. BENZOFURAN¹

(a) Preparation of o-formyl phenoxy acetic acid,

The interaction between o-salicylaldehyde (5 g.) and ethyl bromo acetate (6 g.) took place in boiling acetone (60 cc) containing potassium carbonate (10 g.) over a period of three hours. o-formyl phenoxyacetic ester was thus obtained as colourless prisms melting at $47-48^{\circ}$ C.

Hydrolysis of the ester with 4% aqueous sodium hydroxide for ten minutes gave the desired acid, which was obtained as colourless needles, melting at 132°C., after recrystallization from benzene.

(b) Preparation of benzofuran,

A mixture of the above acid (ten parts by weight) and sodium acetate (28 parts) with acetic anhydride (100 parts) were boiled for one half hour. The mixture was diluted with water and neutralized the next day with sodium bicarbonate. The benzofuran was isolated with ether, and was an almost colourless mobile oil boiling at 132°C. 1, 2, 7, 8 DIBENZACRIDINE³

 β -napthol (5 g.) and β -naphthylamine (5 g.) were melted together at 160°C. Paraformaldehyde (1.5 g.) was gradually added. The latter quickly dissolved with the evolution of water vapour, and the melt became yellow.

The mixture was heated another hour at 200-250°C.

~51-

then it was poured into warm, dilute sodium hydroxide solution. The mixture in the sodium hydroxide solution was boiled up. The dibenzacridine then settled as a yellow granular mass, which was filtered, washed and dried. By recrystallizing this yellow substance several times from toluene, bright yellow needle-like crystals of the dibenzacridine (melting at 216°C) were obtained in good yield.

1, 2, 5, 6, DIBENZACRIDINE^{3'}-

The same method was used as for 1, 2, 7, 8 dibenzacridine except that \checkmark -naphthylamine was condensed with β naphthol.

In this case the yield was rather low, as the thermal condensation resulted in a great deal of tarry material being formed.

The product obtained was recrystallized from toluene, then several times from acetone, giving bright yellow crystals(melting at 228°C).

DIBENZOTHIOPHENE²

Biphenyl (50 g.) and sulphur (21 g.) were melted together in a one litre round bottomed flask, and the temperature raised to $115^{\circ}C$ at the end of the eighth hour. When cooled, the mass in the reaction flask was extracted three times by boiling with 100 cc's of water, then it was cooled and the water decanted each time. Then eight alcohol extractions were made, boiling each time with a litre of alcohol and decanting while hot. The combined extracts were digested with darcocarbon and filtered immediately through a hot Büchner funnel. Upon cooling, almost colourless needles separated from the filtrate.

These crystals were recrystallized from ethanol and chromatographed(melting at 98°). The compound forms a picrate which melts at 125° C.

BIBLIOGRAPHY FOR SYNTHESES

Foster and Robertson, J. Chem.Soc., 921(1939).
 Gilman and Jacoby, J. Org. Chem., <u>3</u>, 108(1938).
 Ullmann and Fetvadgian, Ber. <u>36</u>, 1027(1903).