

Studies on X-Ray Diffraction in Organic Liquids Part I. Cyclic Compounds

By

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Abstract

The X-ray diffraction haloes of organic liquids of various cyclic compounds were investigated by the photographic method. The Shearer metal tube excited by a transformer was, in most of our experiments, employed as a source of X-rays. In the production of the diffraction halo, the liquid molecules may be taken as the centers from which the X-rays are scattered, and the dimensions of the halo will be due to the molecular distance and not to the inter-molecular constitution. It is natural to consider that the molecular constitution of a liquid is more or less characteristic of that liquid according to the form of its molecules, in order that it may have a definite density and compressibility. From these considerations it is to be inferred that spherical molecules will produce a single sharp maximum of intensity in the halo, while molecules of other forms will show their characteristic intensity distribution in the halo. Consequently some suggestions as to the molecular form or the molecular constitution of organic liquids will be obtained by careful observation of the appearance of the halo. Although all haloes may naturally have their own peculiar appearance, they seem to be capable of being roughly classified into five types, which are discussed in the third section.

Next the effect of the different side-chains of the cyclic compounds on the appearance of haloes was observed, and indications were found that the chemical constitutional formulae do not generally show the real molecular form. When, however, we pick out some particular liquids, we are able to find some parallelisms between the change in the figures of the haloes and the atomic constitution of the molecules. Some of these interesting relations are described and discussed in the last part of the present report.

1. General Description

When a narrow pencil of monochromatic X-rays was made to pass through a thin layer of liquid and received on a photographic plate, the X-rays scattered by the liquid gave rise to a more or less sharp circular halo, separated from the direct spot. The observation of this

phenomenon was carried out by Debye and Scherrer¹ in the course of their work on X-ray diffraction by irregularly oriented substances which is known as the powder method of X-ray crystal analysis. As they employed rather complex organic liquid compounds like benzene, they attributed these phenomena to the regular arrangement of the atoms in benzene molecules. Such a broad and diffuse halo seemed to be due to the small number of atoms in the molecules compared with those in the crystal fragments of the powder method. They considered neither the arrangement of the electrons in the atom nor that of the molecules in the liquid.

This suggestion was negated by the investigation of W. H. Keesom and J. De Smedt². They obtained similar photographs with liquid oxygen, nitrogen and argon, which are too simple to compose the diffraction grating. They utilized the opinion advanced by Ehrenfest³ to explain the scattering of a diatomic molecule. According to his calculation, the direction representing a maximum intensity of the scattered radiation by a diatomic molecule could be derived from the following formula,

$$\alpha = \frac{7.72 \lambda}{4\pi \sin \frac{\varphi}{2}} = \frac{\lambda}{1.63 \sin \frac{\varphi}{2}}$$

where α is the distance between two atoms, λ the wave length of the incident radiation and φ the angle of maximum intensity to the incident ray. Keesom and Smedt applied this formula to the arbitrarily restricted two neighbouring molecules and calculated the molecular distance α by using the above formula. They also calculated theoretically the molecular distances α on the special assumption that the molecules in a liquid possess the hexagonal closest packed arrangement of a sphere, and obtained some agreement between the theoretical and the experimental values. On this assumption,

$$\alpha = 1.33 \sqrt[3]{\frac{M}{\rho}} A.U. = 1.123 \sqrt[3]{\frac{m}{\rho}} \text{cm.}$$

where M is the molecular weight, ρ the density of the liquid and m the mass of the liquid molecule, taking that of one hydrogen atom as

1 Debye and Scherrer, *Nachrichten*, Göttingen. **16**, 16, (1916).

2 Keesom and Smedt, *Proc. Sect. of Science (Amsterdam)* **25**, 118, and **26**, 112, (1923).

3 Ehrenfest, *Proc. Sect. of Science (Amsterdam)* **17**, 1184, (1915).

1.663×10^{-24} gms. Another view was put forward by Hewlett¹ who observed the same phenomena by the ionization method. He suggested that ordinary liquids possess something resembling crystal structure or large groups of regularly arranged atoms. Notwithstanding that the explanation of the observed facts could be simply understood, this idea was said by Raman and Ramanathan², who proposed another interesting idea, to be somewhat artificial. Their opinion depends on the consideration that the positions of the molecules in liquids are not at random but possess a certain degree of regularity which can be estimated thermodynamically from the compressibility of the liquid. In the case of X-ray scattering the wave-length of which is very small, the maximum intensity of the scattered radiation will occur in the direction θ given by the following equation,

$$\lambda = 2\lambda_0 \sin \frac{\theta}{2}$$

where λ is the wave-length of the incident X-ray and λ_0 the mean molecular distance. This calculation concerns spherical molecules and we have a single maximum whose sharpness depends on the compressibility of the liquids.

On the other hand, when the molecules have not a spherical form but a cylindrical or a flat disc form, they will give a diffraction halo of different appearance even though they possess asymmetry in the internal structure of their scattering centers, namely the electrons, and hence in considering the distances between two molecules, one can only take the positions of their geometrical centers. Especially when the distribution of the scattering centers in the molecules i.e. the electrons is unsymmetrical, the appearance of the diffraction halo will show more complexity because the important point in the molecule, so far as molecular scattering is concerned, will never coincide with the geometrical center, but be shifted towards the point where there is a comparatively dense aggregation of the electrons. Thus the structure of the liquid-halo depends in a great measure on the form and symmetry of the molecules. Sogani³ discussed this problem rather conclusively. As he stated, it seems natural to consider that so far as the manner of molecular packing is concerned, a liquid has much more in common

¹ Hewlett, *Phys. Rev.* **20**, 688 (1922).

² Raman and Ramanathan, *Proc. Ind. Ass. f. Cult. of Sci.* **8**, 127 (1923).

³ Sogani, *Ind. Jour. Phys.* **1**, 357 (1927) and **2**, 97 (1927).

with solids than with gases. The complete randomness of molecular distribution peculiar to a gas is the result of its low density. In other words, it is due to the fact that the actual space occupied by the molecules is very small in comparison with its total volume. In the case of a liquid, however, its high density and low compressibility indicate that the molecules must be distributed in a fairly regular manner, as regards spacing, especially when the shape of the molecules departs from the spherical; because in order that the chaotic distribution may be possible, the space in the liquid per molecule must be at least equal to the volume of the sphere having a diameter equal to the longest dimension of the molecules. But this is not true in actual cases. Thus in a liquid having molecules of unsymmetrical shape, there is a sensible orientative influence of neighbouring molecules on each other tending to cause the molecules to diminish the space occupied by them. Therefore such unsymmetrical molecules will have a definite orientation in the liquid in order to have a definite density and compressibility, and the diffraction haloes obtained with these liquids will have a characteristic appearance.

If we take as a simple example, the elongated or cylindrical molecule, and the flat molecule, which means the flat circular disc shape, we can have the following two kinds of arrangement which represent equally dense packing under the actual conditions at ordinary temperatures.

The neighbouring molecules are more or less parallel and placed nearly end to end as in the solid state, and in one case the orientation alters only gradually from molecule to molecule, but in the other case, a very abrupt change in orientation occurs very often. The latter is perhaps more arbitrary than the former, which seems to be very probable. In both cases, the diffraction halo possesses two maximum intensities, the one corresponding to the length of the cylindrical molecule or the diameter of the flat molecule, and the other corresponding to the diameter of the cross-section of the former or the thickness of the latter. The relative intensity of the two maxima will, however, be quite different according to the manner of the orientation as well as the shape of the molecules, which may be considered for each case in the last section.

2. Experimental Part

The powder photographic method of Debye and Scherrer was

employed in the present experiment, a thin layer of liquid, instead of powdered crystals, being placed in the same position. As the source of X-rays, chiefly a Shearer metal tube with copper anticathode, but sometimes the Coolidge tube with molybdenum anticathode, was employed. In the case of the former tube, it was evacuated with a molecular pump during the whole time of exposure and excited with a transformer; the working voltage was kept at about 50 k.v., but the current in the tube could unfortunately not exceed 2.5 milliamperes because of the small capacity of the transformer. The Coolidge tube was excited with an induction coil working with a mercury gas interrupter, the exciting voltage being about 70 k.v. and the current through the tube about 2 milliamperes. Under these conditions, the X-rays were fairly monochromatic, consisting mainly of K_{α} and K_{β} lines and for the purpose of the present work, it seemed to be unnecessary to use a filter to cut off the K_{β} line. In order to contain the liquids the authors used an excessively thin glass tube 1.5 mm. in diameter, except in the case of liquids of high density which contained sulphur, chlorine or bromine. These liquids did not give the diffraction halo with such a glass tube on account of their great absorbing power, and therefore, a vessel of about 0.3 mm. in thickness and having a thin mica window for the X-ray beam was passed, as was suggested by Sogani. This vessel was also employed for some other liquids and it was found that the appearance of the diffraction halo did not show any difference from that obtained with the glass tube.

The X-rays radiated from the Shearer tube were made to pass through two circular slits of about 2 mm. diameter and separated from each other by about 4 cm., and then strike the specimen. The photographic plate was always placed behind the specimen at a distance of 2.91 cm. The time of exposure were mainly 3 hours but sometimes 4 hours.

For the Coolidge tube, the diameter of the two circular slits was 1.5 mm, the distance between them 3.5 cm. and that between the photographic plate and the specimen 4.82 cm. The time of exposure was about 30 hours. The specimens marked + in the next section were Kahlbaum's make and those marked * Merk's. The remainder, which have no mark were obtained from the organic chemistry research laboratory in our College; some of them were not very pure, but seemed to be sufficiently so for the purpose of the present research.

3. Experimental Results and Discussion

As stated in the previous section, it is natural to consider that the diffraction halo is due solely to the arrangement of the molecules in the liquid, and not at all to the inner molecular structure. The following experiment seems to afford reliable proof of this opinion. A mixture of two liquids which would give different diffraction haloes, gives another characteristic figure, and does not show the superposition of one above the other. Figs. 48, 49, 50 and 51 of Plate IV are reproductions of the photographs obtained with the mixtures of equal volumes of two liquids, benzene and nitrobenzene, benzene and decaline, nitrobenzene and cyclohexane, pyridine and tetraline respectively, and Figs. 1, 13, 47, 37, 39 and 46 of Plates I, II, III and IV are those of benzene, nitrobenzene, decaline, cyclohexane, pyridine and tetraline respectively. The name of the liquid is written above each figure.

By glancing at these figures we can easily recognize the following facts, which are summarized in Table I;

1. The benzene-halo has a feeble but distinct scattering outside the sharp principal halo, while the inner region shows comparatively little scattering. The nitrobenzene-halo is very broad and has no sharp maximum in it. The halo for the mixture of these two liquids looks essentially like the nitrobenzene-halo, but is much smaller in size. The radii of the haloes are given in Table I.
2. Though the decaline-halo is more or less diffuse compared with the benzene-halo, yet it can be classified as a sharp one. The size is much smaller and the outside scattering of the benzene-halo can not now be recognized. The halo for the mixture of benzene and decaline is accompanied by a recognizable outside scattering as in the case of benzene and the principal halo is midway between those of the components in size.
3. The cyclohexane-halo is sharp and something like the benzene halo though its outer scattering is much fainter. When nitrobenzene, the halo of which is very broad, is mixed with it, the halo becomes rather diffuse and the outer scattering becomes less faint.
4. The tetraline-halo is broad and diffuse like that of nitrobenzene, and the pyridine-halo rather sharp accompanied by a feeble but distinct outside scattering as in the case of benzene. The mixture of these liquids gives a halo resembling that of tetraline but much

Table I

Name of liquid	Radius of max. intensity	Radius of inner limit	Radius of outer limit
Benzene	0.94 ^(cms)	0.75 ^(cms)	1.73 ^(cms)
Nitrobenzene	1.02	0.51	1.45
Mixture of the above two	0.76	0.48	1.15
Benzene	0.94	0.75	1.73
Decaline	0.76	0.49	1.05
Mixture of the above two	0.85	0.51	1.28
Nitrobenzene	1.02	0.51	1.43
Cyclohexane	0.87	0.63	1.10
Mixture of the above two	0.93	0.62	1.86
Tetraline	0.80	0.48	1.25
Pyridine	0.98	0.68	1.85
Mixture of the above two	0.86	0.48	1.12

Table II

Name of liquid	θ_{Cu}	d_{Cu} (A.U.)	θ_{Mo}	d_{Mo} (A.U.)
Benzene	17°54'	4.93	8°22'	4.90
Benzylalcohol	17°10'	5.15	8°14'	4.99
Pyridine	18°38'	4.75	8°39'	4.72
Nitrobenzene	19°20'	4.57	9°12'	4.44
Aniline	17°10'	5.15	8°14'	4.99

Bragg's formula

$$\lambda = 2d \sin \frac{\theta}{2}$$

where θ represents the scattering angle, and λ the wave-length of the incident X-ray; 1.54 A.U. for the K-lines of copper and 0.712 A.U. for those of molybdenum. This d suggests the mean molecular distances in the theory of Raman and Ramanathan, or the spacings in the molecular groups in the theory of Hewlett and others. θ_{Cu} and d_{Cu} are given in the case of copper lines, and θ_{Mo} and d_{Mo} , molybdenum lines. Considering that the results obtained with molybdenum lines can hardly be accurate on account of their small scattering angle, the disagreement between d_{Cu} and d_{Mo} seems to lie within the limits of experimental error.

Now we shall proceed to discuss the appearance of the diffraction

smaller in size.

Next the size of the halo changes proportionately with the wave-length of the incident X-ray and shows conclusively that the spacing of the molecules in the liquid does not change with the wave-length. This was tested by employing the K-lines of copper and molybdenum and the results are summarised in Table II. Some of the photographs taken with the K-lines of molybdenum are reproduced in figures 52-56 in Plate IV.

θ_{Cu} and θ_{Mo} are the scattering angles, and d_{Cu} and d_{Mo} the spacings for the principal halo calculated from

halo of each liquid. All the photographs were taken with the K-lines of copper and are reproduced in figures 1-47 in Plates I, II, III and IV. In spite of all the figures showing individual peculiarities, they seem, by careful observation, to be capable of being divided into five types;

Type A. The halo having a considerable scattering outside the principal halo and that in the inner region being very slight. In this type there are two classes A_1 and A_2 , one having a marked discontinuity between the principal halo and the outer scattering, the other showing continuous decrease of intensity from the former to the latter. The molecules having two principal dimensions are in our opinion so arranged that the smaller dimension is more distorted than the larger one. The haloes of benzene, aniline, toluene, phenylhydrazine, chlorobenzene, anisol, phenylmustardoil, diphenylether, ortho, meta, para-cresol, ortho, meta-toluidine, ortho, meta, para-xylene, cymene, cyclohexene, cyclohexylamine and pyridine belong to this type.

Type B. The halo having a considerable scattering inside the principal halo and a very slight scattering in the outer region. There seems to be also two classes, B_1 and B_2 , the one having a feeble maximum in the scattering in the inner region and the other, no maximum. The molecules having two principal dimensions are in this case so arranged that the larger dimension is more distorted than the other. The haloes of monomethylaniline, acetophenone, dimethylaniline, ethylaniline, ethylbenzoate diethyl-aniline, isoamylbenzoate belong to this type.

Type C. The halo having scatterings of about equal intensity on both sides of the principal halo. The figures of this type show many different appearances, but they can roughly be divided into two classes C_1 and C_2 ;

C_1 is a broad and more or less uniformly bright halo. It is very difficult to ascertain the maximum intensity. C_2 is a broad halo but the maximum position can be observed with some certainty. The molecules having two principal dimensions are in this case so arranged that both are equally distorted from the regular orientation. The haloes of benzonitrile, benzaldehyde, benzylalcohol, thiophenol, nitrobenzene, benzylchloride, bromobenzene, anisaldehyde, carvacrol, furfurol, quinoline, para-methyl-quinoline and tetraline belong to this type.

Type D. A single sharp halo having a very faint scattering on both sides. The form of the molecule will be spherical and the haloes of cyclohexane, thiophene, pyrrol and decaline belong to this type.

Type E. The halo having two distinct maxima of nearly equal intensity. The molecules probably have two principal dimensions and are regularly arranged. The haloes of ortho-nitrotoluene, mesitylene and piperidine belong to this type.

The class to which each figure may belong is given in the column marked "appearance" in all the tables below, and the graphs shown in the same column, are given in order to provide a rough idea of the intensity distribution in the haloes. The scattering angle θ for the direction of maximum intensity in the halo, is given in the next column. Where the halo shows two maxima, the values for both of them will be found in this column. In the case of some figures, it is, of course, more or less difficult to determine the class to which they may belong. This characteristic of the appearance is caused by the form of the liquid molecule or the unsymmetrical distribution of electrons in it or both, because the distribution of the scattering center of the molecules in liquids must depend on these factors.

It was stated in the first section that the spherical molecules the scattering center of which coincides with the geometrical center give a single sharp halo, as was mentioned by Raman. This will correspond to the halo of type D. When the cylindrical or flat circular molecules are arranged in the liquid state so as to have a density not differing from the solid state, the distribution can not be quite at random but somewhat regular, and then the halo will have two maximum intensities corresponding to the two principal dimensions of the molecules i.e. the diameter of the cross-section, the length of the molecules for the former and the diameter of the flat surface, the thickness for the latter. This is the case for type E. The manner of the regular distribution is peculiar to each liquid and they all differ from each other. If the regularity with regard to one principal dimension is more prominent than that of the other, the halo shows one distinct maximum having a marked scattering at one side of it. This is the case with types A and B. When the regularity with regard to both dimensions is equally distorted, the halo does not show a distinct maximum, as is shown in type C. This consideration may be roughly applied to the cyclic compounds and their derivatives as above mentioned. In the column marked "spacing" the value of d calculated from Bragg's formula

corresponding to the maximum intensity, the inner and outer limits to which the halo extends are given respectively. When the inner or outer scattering is too slight to allow of this limit being determined, these data are, of course, absent. The values d (Smedt) given in the next column are calculated from Ehrenfest's formula. The values of both $\sqrt[3]{\frac{m}{\rho}}$ and $1.123 \sqrt[3]{\frac{m}{\rho}}$ are also given in all the tables, where m is the mass of a molecule of the liquid and ρ its density. The former will show the length of the edge of the cubic volume which may be occupied by a molecule and give a rough idea of the average size of the molecule, and the latter will show the molecular distance when the molecules are assumed to have the hexagonal closest packed arrangement of a sphere. The coincidence of d (Smedt) and $1.123 \sqrt[3]{\frac{m}{\rho}}$ obtained by Keesom and Smedt seems to be accidental in this case, as noted by Sogani.

The third column gives the number of electrons added to the benzene molecule, which will roughly show the unsymmetricality of the molecule. The various benzene derivatives having one, two and three branches are summarised in Tables III and IV, and the other cyclic compounds and their derivatives in Table V respectively. By examining those tables and the annexed figures and keeping the above considerations in mind we can have at once some idea of the form or arrangement of each molecule in the liquid. We can not find any regular change in the dimensions or the size of haloes corresponding to the number of additional atoms or electrons in the side chains. However, all the cyclic compounds having no branches, like benzene, pyridine, cyclohexane, pyrrol, thiophene, decaline and quinoline, give a sharp halo accompanied by little scattering.

If they have some atoms in their branches their haloes become more and more diffuse according to the nature of the additional atoms. Although aniline and nitrobenzene have three atoms at one corner of the benzene ring, their haloes are quite different; the former halo is much finer than the latter. Diphenyl-ether and iso-amylbenzoate have much more complex branches than nitrobenzene and chlorobenzene, but the haloes of the former compounds are finer than those of the latter. This seems to indicate clearly that the real forms of molecules are quite different from the structural formula.

The parallelism between diffuseness of halo and increase of density is more or less marked, except in the case of some exceptional liquids.

Generally, the compounds having any atom of comparatively high atomic weight like chlorine, bromine or sulphur give very diffuse haloes. (The density of these liquid is, in general, great.) However, if we pick out some peculiar compounds, there seems to be found some interesting relations as described below. For example when we take out the compounds which have the same number of atoms in a side chain, the sharper halo will be given by those having fewer electrons. And also, when we take out the ones having the same number of electrons in a side chain, the sharper halo will be obtained from those having more atoms. This statement agrees for the most part with the assertion that the sharper halo will be given by the compounds of less density. The above relations hold for compounds accompanied by only one branch, and if we consider the case of those having two or more branches the relation may be naturally more complex. By comparing the haloes of benzene, chlorobenzene, bromobenzene; benzonitrile, thiophenol; aniline, benzaldehyde, nitrobenzene, phenylmustardoil; toluene, benzylchloride, benzylalcohol, phenylhydrazine, anisol; dimethylaniline and monoethylaniline, respectively, the former case will be recognized, and in the haloes of aniline, toluene; chlorobenzene, thiophenol, anisol, phenylhydrazine, benzylalcohol, monomethylaniline; nitrobenzene, acetophenone; benzylchloride, dimethylaniline, monoethylaniline, the latter case will be found.

Now we shall proceed to discuss the haloes of some more particular compounds. Our description will deal with the position of maximum intensity, the limits of appreciable scattering and the manner of intensity distribution within these limits.

1. *Benzene, toluene, xylene, mesitylene and cymene.* The benzene-halo has a feeble but distinct scattering outside the principal halo with a marked discontinuity between them (Class A₁). The outside scattering is gradually increasing in the toluene-halo and the discontinuity becomes vague (Class A₂). This peculiarity is more prominent for three xylenes, especially in the case of meta-xylene the principal halo can scarcely be found (Class A₂). Finally, the mesitylene halo shows two comparatively sharp and narrow maxima of nearly equal intensity (Type E). Although cymene has four CH₃ groups, they form two branches and its halo is resemble the xylene halo belonging to class A₂ and is quite different from the mesitylene type.
2. *Benzene, aniline, phenylhydrazine, monomethylaniline, dimethyl-*

aniline, monoethylaniline, diethylaniline and toluidine. The aniline halo is essentially like the benzene halo accompanied by a comparatively stronger scattering outside the principal halo (Class A₁). The phenylhydrazine-halo has a still stronger outside scattering showing an indistinct boundary like the toluene-halo, but in this case the scattering in the inner region is more or less marked (Class A₂). The monomethylaniline halo has more inner scattering and somewhat poor outside scattering (Class B₁). The dimethylaniline halo shows still more inner scattering (Class B₂). We can, however, find a space around the direct position where the scattering is scarcely observed. In the monoethylaniline and the diethylaniline halo, the inner scattering extends and almost reaches the direct spot and shows even a small maximum of intensity near it (Class B₂). Although toluidine has the same number of atoms as monomethylaniline, they form two branches and its halo has quite a different appearance from that of the latter belonging to Class A₂.

3. *Cresol, toluidine, and xylene.* All these compounds have three isomers and their haloes show a comparatively sharp principal maximum of intensity accompanied by a moderate outside scattering (Class A₂). Notwithstanding that the intensity distributions in the haloes of ortho- and para-compounds resemble each other, those of the ortho-compounds show, on careful observation, a clearer boundary between the principal halo and the outer scattering than those of para-compounds. In the haloes of meta-compounds, the boundary of the principal halo is less marked, especially in the meta-xylene-halo. The spacings corresponding to the maximum intensity for meta compounds are considerably smaller than in the other two. These seem to be characteristic of meta-compounds. The spacings corresponding to the para-compounds are somewhat smaller than those of the ortho-compounds. It must be noted that the order mentioned above is unaltered for all ortho-meta- and para-compounds in the present experiment. The ortho-nitrotoluene-halo has two maxima of nearly equal intensity (type E).
4. *Tetraline, decaline; pyridine, piperidine.* The tetraline halo is a rather diffuse and broad band. It is somewhat difficult to determine the position of its maximum intensity (Class C₁). The decaline halo, however, is a rather sharp ring having very little

and hardly observable scattering in the outer and inner region (type D). This shows that the decaline molecule is, according to our opinion, a typical spherical molecule, like the cyclohexane molecule. The pyridine-halo has a comparatively large inner scattering belonging to class C_2 . The piperidine halo, however, has two maxima of nearly equal intensity (type E). The decaline halo is much smaller than the tetraline halo, and is the same as in the case of the piperidine- and the pyridine-halo. Decaline and piperidine molecules can be derived from the tetraline and pyridine molecules by adding six hydrogen atoms in somewhat similar manner respectively. This seems to be the origin of the difference.

5. *Pyridine, Quinoline; Cyclohexane, Tetraline.* The appearance of all these haloes has been already mentioned. It will be noticed at once that the quinoline- and tetraline-haloes are much more diffuse than those of pyridine and cyclohexane. The molecules of the former can be derived from the latter molecules by adding four carbon and four hydrogen atoms in like manner. This is the only cause of the difference in the intensity distribution.

In conclusion the writers wish to express their best thanks to Prof. S. Komatsu and Mr. R. Nakai who have kindly supplied many samples required for these investigations.

Table III

Name of liquid	Rational formula	No. of electrons added to benzene	Appearance		θ for max. intensity	Spacing, $d = \frac{\lambda}{2 \sin^2 \frac{\theta}{2}}$ (A.U.)			$d_{\text{Smect}} = \frac{\lambda}{1.63 \sin^2 \frac{\theta}{2}}$ (A.U.)	Density ρ	$\frac{3}{\sqrt{m}} \sqrt{\frac{m}{\rho}}$ (A.U.)	$\frac{1.123}{\sqrt{m}} \sqrt{\frac{m}{\rho}}$ (A.U.)
			Intensity curve	Type		Max. intensity	Inner limit	Outer limit				
Benzene*	C_6H_6	0		A ₁	17° 54'	4.93	6.12	2.91	6.04	0.879	5.29	5.94
Aniline*	$C_6H_5NH_2$	8		A ₁	17° 10'	5.15	8.56	3.21	6.30	1.015	5.34	6.00
Toluene*	$C_6H_5CH_3$	8		A ₂	16° 8'	5.51	9.06	4.03	6.75	0.866	5.61	6.30
Benzonitrile*	C_6H_5CN	12		C ₂	17° 54'	4.93	8.85	3.46	6.04	1.005	5.55	6.23
Benzaldehyde*	C_6H_5CHO	14		C ₁	15° 54'	5.58	9.06	4.03	6.82	1.049	5.52	6.20
Benzylalcohol†	$C_6H_5CH_2OH$	16		C ₂	17° 10'	5.15	8.85	3.62	6.30	1.046	5.56	6.25
Phenylhydrazine†	$C_6H_5NHNH_2$	16		A ₂	17° 22'	5.10	8.56	3.96	6.25	1.098	5.47	6.14
Monomethylamine	$C_6H_5NHCH_3$	16		B ₂	18° 4'	4.90	8.85	3.69	6.00	0.990	5.65	6.34
Chlorobenzene†	C_6H_5Cl	16		A ₂	17° 26'	5.06	7.70	3.48	6.20	1.106	5.53	6.21
Thiophenol†	C_6H_5SH	16		C ₁	17° 6'	5.14	7.85	3.48	6.28	1.081	5.53	6.21
Anisol†	$C_6H_5OCH_3$	16		A ₂	17° 54'	4.93	7.62	3.82	6.03	0.987	5.67	6.36
Acetophenone	$C_6H_5COCH_3$	22		B ₂	18° 48'	4.73	9.89	3.48	5.80	1.030	5.79	6.50
Nitrobenzene*	$C_6H_5NO_2$	22		C ₁	19° 20'	4.57	8.85	3.41	5.59	1.203	5.54	6.22
Dimethylaniline†	$C_6H_5N(CH_3)_2$	24		B ₂	16° 8'	5.51	9.28	3.10	6.75	0.958	5.95	6.68
Ethylaniline	$C_6H_5NH_2C_2H_5$	24		B ₂	19° 0'	4.67	9.06	3.44	5.70	0.963	5.94	6.67
Benzylchloride*	$C_6H_5CH_2Cl$	24		C ₂	17° 56'	4.94	7.20	3.55	6.05	1.103	5.76	6.47
Phenylmethylol	C_6H_5SCN	28		A ₂	19° 30'	4.56	6.02	3.23	5.57	1.135	5.83	6.55
Bromobenzene†	C_6H_5Br	34		C ₁	18° 52'	4.70	6.02	3.23	5.75	1.495	5.59	6.28
Ethylbenzoate	$C_6H_5CO_2C_2H_5$	38		B ₁	19° 30'	4.56	8.85	3.55	5.57	1.051	6.19	6.95
Diethylaniline	$C_6H_5N(C_2H_5)_2$	40		B ₂	18° 16'	4.84	8.56	3.36	5.92	0.939	6.42	7.21
Diphenylether	$C_6H_5OC_6H_5$	48		A ₁	18° 38'	4.75	6.94	3.96	5.82	1.073	6.41	7.20
Isoamylbenzoate	$C_6H_5CO_2C_5H_{11}$	62		B ₂	18° 38'	4.75	—	3.33	5.82	0.993	6.85	7.69

Table IV

Name of liquid	Rational formula	No. of electrons added to benzene	Appearance		θ for max. intensity	Spacing, $d = \frac{\lambda}{2 \sin \frac{\theta}{2}}$ (A.U.)			$\frac{d_{\text{Smectt}}}{\lambda} = \frac{1}{1.63 \sin^2 \theta}$ (A.U.)	Density ρ	$\frac{\sqrt{m}}{V \rho}$ (A.U.)	$\frac{1.123 \sqrt{m}}{V \rho}$ (A.U.)
			Intensity curve	Type		Max. intensity	Inner limit	Outer limit				
Ortho-cresol	$C_6H_4(OH)CH_3$	16		A ₂	16°38'	5.31	7.62	2.98	6.50	1.046	5.56	6.24
Meta-cresol	"	"		A ₂	18° 4'	4.90	7.62	3.21	6.00	1.035	5.58	6.27
Para-cresol	"	"		A ₂	16°50'	5.28	8.38	3.18	6.45	1.031	5.58	6.27
Ortho-xylene	$C_6H_4(CH_3)_2$	16		A ₂	15°54'	5.58	9.05	3.33	6.82	0.863	5.89	6.61
Meta-xylene	"	"		A ₂	18° 4'	4.90	9.06	3.36	6.00	0.862	5.89	6.61
Para-xylene	"	"		A ₂	17° 0'	5.20	8.85	3.30	6.35	0.861	5.90	6.62
Ortho-toluidine+	$C_6H_4(NH_2)CH_3$	16		A ₂	16°50'	5.28	7.70	3.23	6.45	1.003	5.62	6.31
Meta-toluidine+	"	"		A ₂	17°10'	5.15	8.56	3.41	6.30	0.992	5.64	6.33
Ortho-nitrotoluene	$C_6H_4(NO_2)CH_3$	30		E	{11°54' 21°58'}	7.40 4.04	—	3.08	{8.79 4.93}	1.662	5.16	5.80
Anisaldehyde+	$CH_3O C_6H_4 CHO$	30		C ₁	17°54'	4.93	9.89	3.26	6.04	1.123	5.86	6.58
Cymene	$CH_3 C_6H_4 CH(CH_3)_2$	32		A ₂	15°14'	5.80	9.06	3.50	7.08	0.865	6.37	7.15
Mesitylene	$C_6H_3(CH_3)_3$	24		E	{11°30' 23°24'}	7.70 3.78	—	—	{9.40 4.60}	0.859	6.14	6.90
Carvacrol*	$C_3H_7 C_6H_3 OH CH_3$	40		C ₂	15°22'	5.74	10.00	4.43	7.00	0.981	6.34	7.12

Table V

Name of liquid	Rational formula	Appearance		θ for max. intensity	Spacing, $d = \frac{\lambda}{2\sin\frac{\theta}{4}}$ (A.U.)			$d_{\text{Svedt}} = \frac{\lambda}{1.63\sin^2\theta}$ (A.U.)	Density ρ	$\sqrt[3]{\frac{m}{\rho}}$ (A.U.)	$\sqrt[3]{\frac{m}{\rho}}$ (A.U.)
		Intensity curve	Type		Max. intensity	Inner limit	Outer limit				
Cyclohexene	C_6H_{10}		A ₁	16° 48'	5.28	7.70	3.20	6.45	0.812	5.52	6.20
Cyclohexane	C_6H_{12}		D	16° 38'	5.31	7.27	4.28	6.49	0.781	5.64	6.33
Cyclohexylamine	$C_8H_{11}NH_2$		A ₁	17° 10'	5.15	7.00	3.55	6.30			
Pyridine*	C_5H_7N		A ₁	18° 38' 8° 26'	4.75 10.42	6.70	2.76	5.82 12.75	0.975	5.13	5.68
Piperidine*	$C_5H_{11}N$		E	17° 32'	5.06	—	3.99	6.18	0.860	5.48	6.15
Furfural*	C_4H_3OCHO		C ₂	17° 0'	5.20	8.56	3.46	6.35	1.159	5.16	5.80
Thiophene+	C_4H_4S		D	18° 40'	4.75	6.26	3.73	5.82	1.071	5.07	5.70
Pyrryl*	C_4H_5N		D	19° 34'	4.56	8.56	3.21	5.57	0.948	4.90	5.50
Quinoline	C_8H_7N		C ₁	18° 38'	4.75	8.56	3.26	5.82	1.095	5.81	6.53
Para-methyl-quinoline	C_8H_9N		C ₁	16° 16'	5.46	10.00	3.78	6.67			
Tetraline	$C_{10}H_{12}$		C ₂	15° 22'	5.75	9.40	3.82	7.02	0.978	6.11	6.86
Decaline	$C_{10}H_{18}$		D	14° 40'	6.02	9.28	4.45	7.35	0.877	6.37	7.15

Plate I

Fig. 1. Benzene.

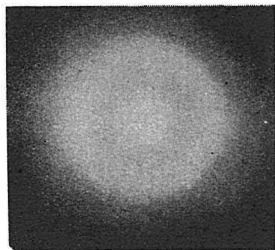


Fig. 4. Benzotrile.

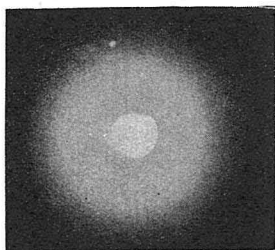


Fig. 7. Phenyl hydrazine.

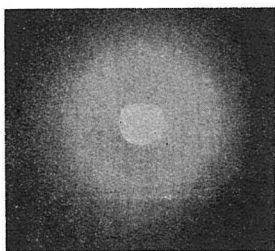


Fig. 10. Thiophenol.

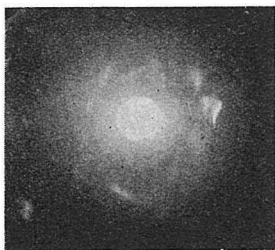


Fig. 13. Nitrobenzene.

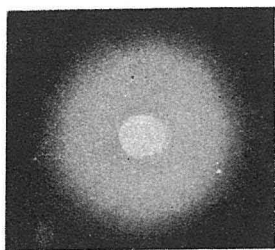


Fig. 2. Aniline.

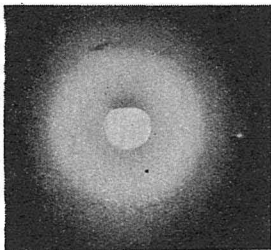


Fig. 5. Benzaldehyde.

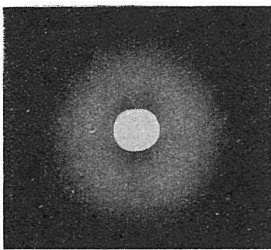


Fig. 8. Monomethylaniline.

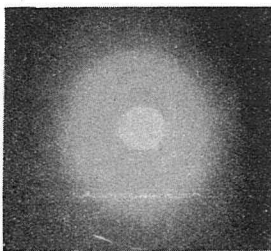


Fig. 11. Anisol.

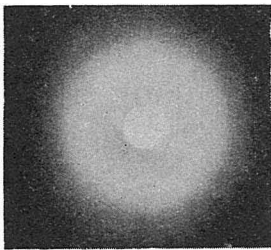


Fig. 14. Dimethylaniline.

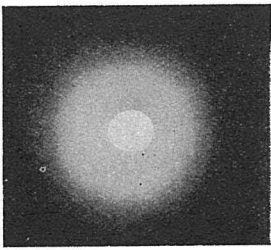


Fig. 3. Toluene.

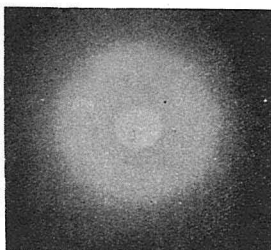


Fig. 6. Benzyl alcohol.

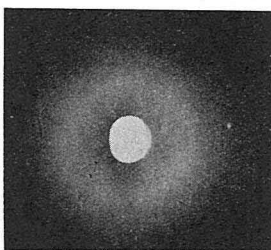


Fig. 9. Chlorobenzene.

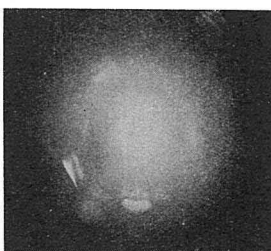


Fig. 12. Acetophenone.

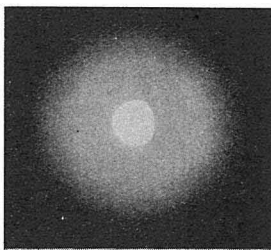


Fig. 15. Ethyl aniline.

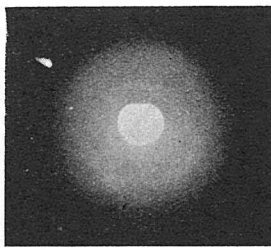


Plate. II

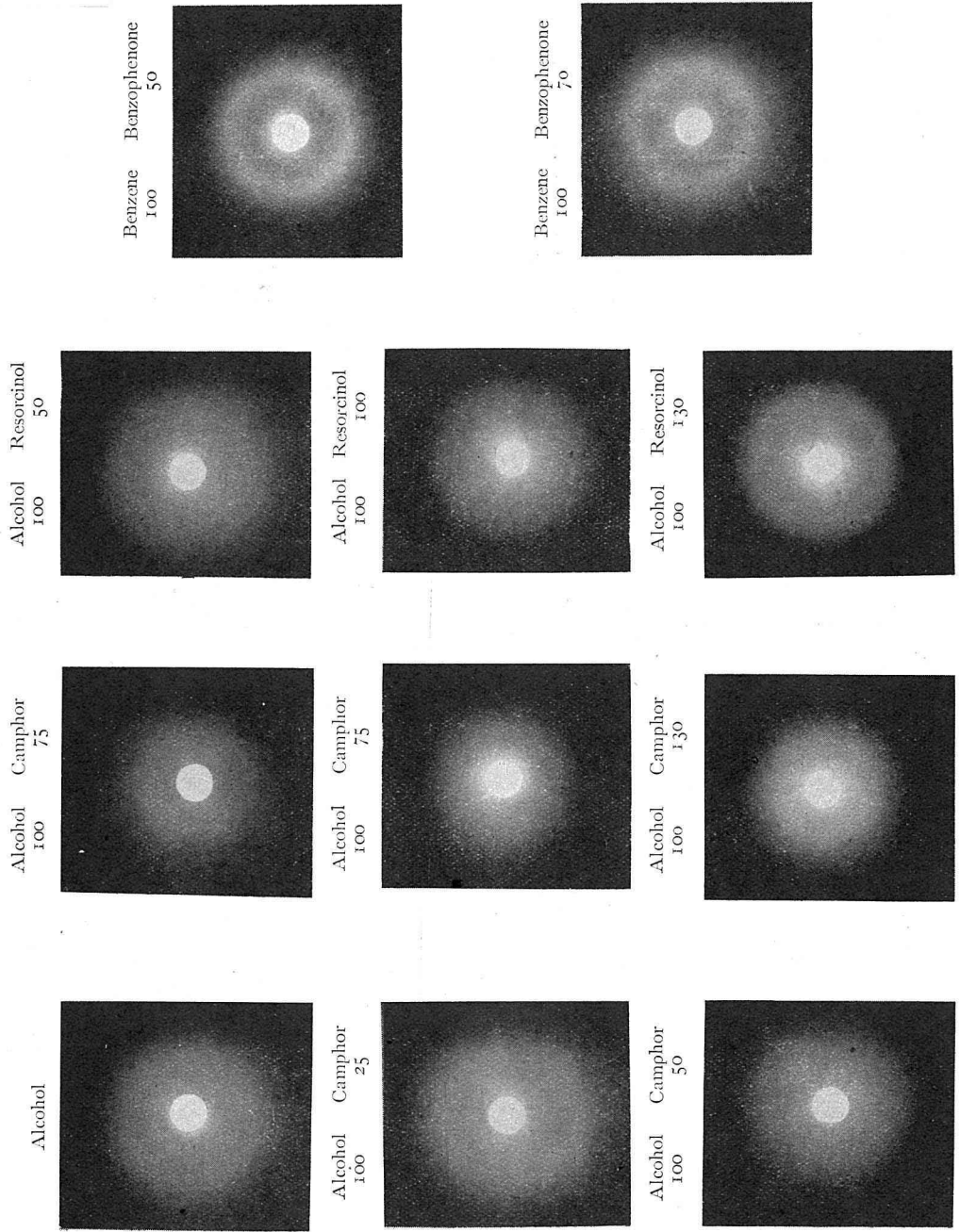


Plate II

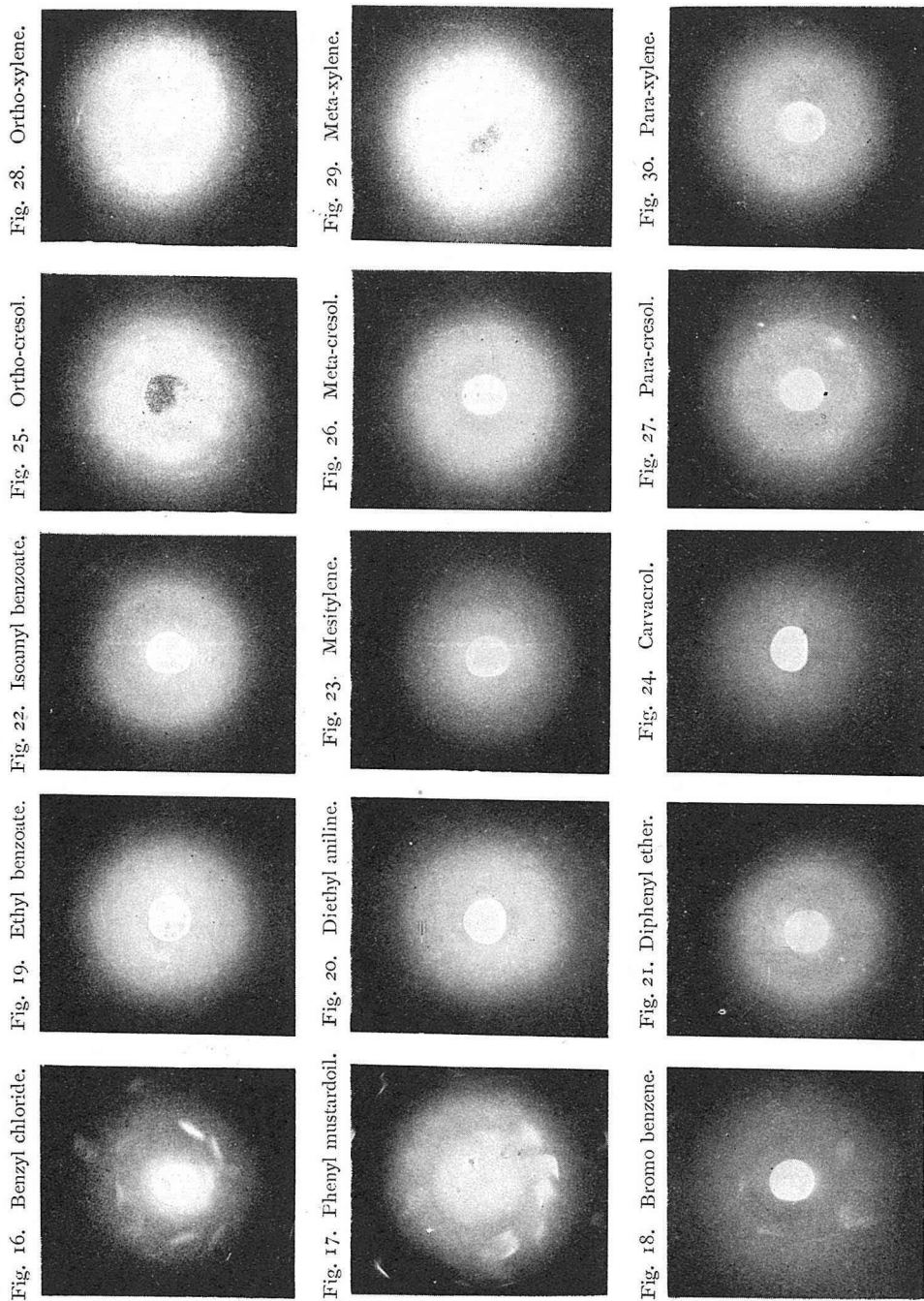


Plate III

Fig. 31. Ortho-toluidine.

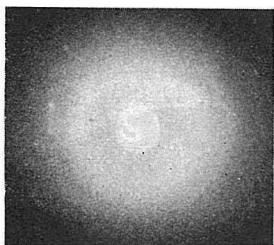


Fig. 34. Anisaldehyde.

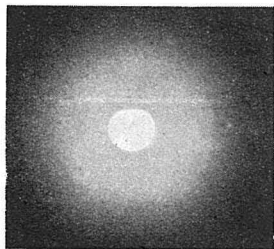


Fig. 37. Cyclohexane.

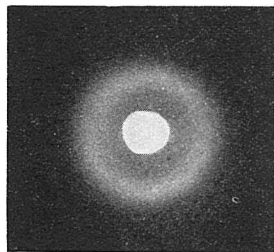


Fig. 40. Piperidine.

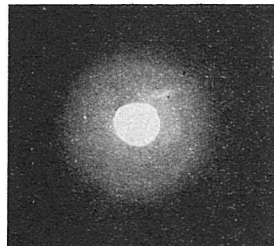


Fig. 43. Pyrrol.

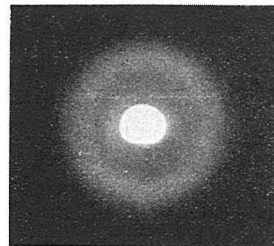


Fig. 32. Meta-toluidine.

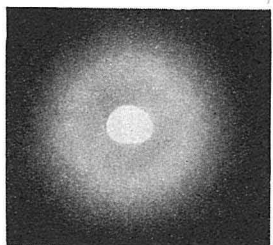


Fig. 35. Cymene.

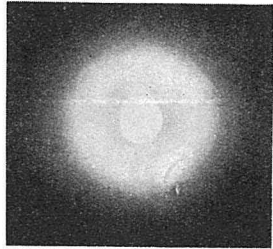


Fig. 38. Cyclohexylamine.

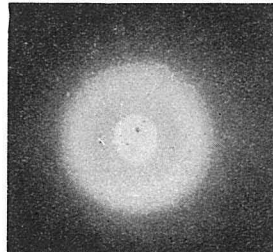


Fig. 41. Furfural.

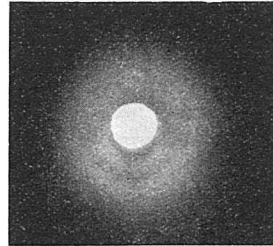


Fig. 44. Quinoline.

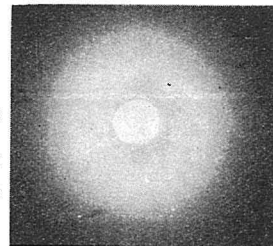


Fig. 33. Ortho-nitrotoluene.

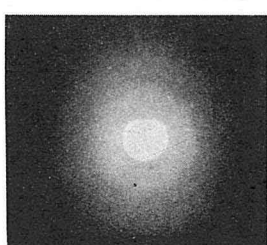


Fig. 36. Cyclohexene.

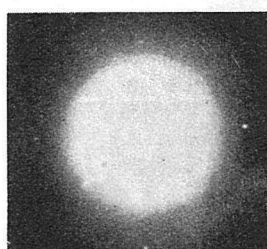


Fig. 39. Pyridine.

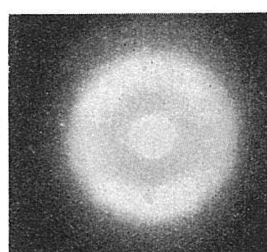


Fig. 42. Thiophene.

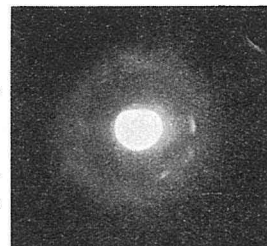


Fig. 45. Para-methylquinoline.

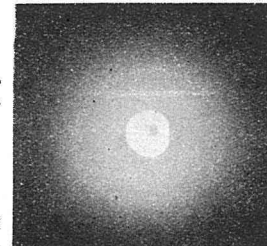


Plate IV

Fig. 46. Tetraline.

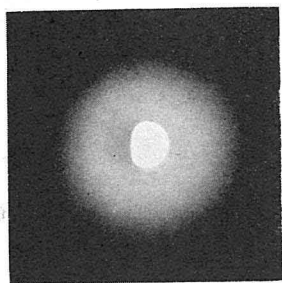


Fig. 47. Decaline.

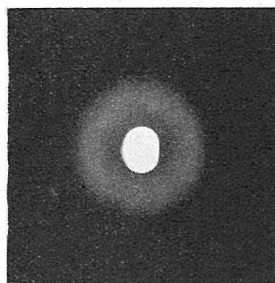


Fig. 48. Mixture of Benzene and Nitrobenzene.

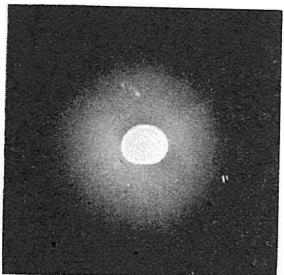


Fig. 49. Mixture of Benzene and Decaline.

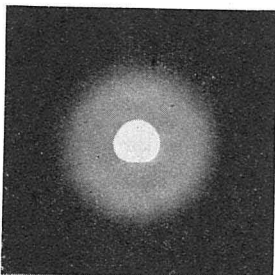


Fig. 50. Mixture of Nitrobenzene and Cyclohexane.

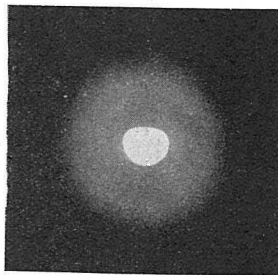


Fig. 51. Mixture of Tetraline and Pyridine.

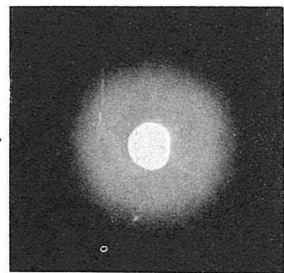


Fig. 52. Benzene.

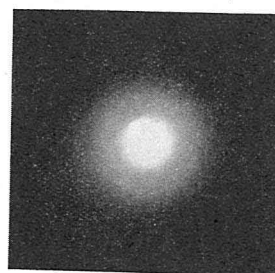


Fig. 53. Benzyl chloride.

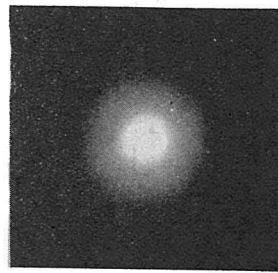


Fig. 54. Pyridine.

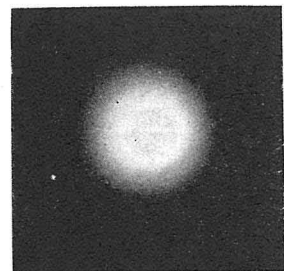


Fig. 55. Nitrobenzene



Fig. 56. Aniline.

