compounds, aniline black and of synthetic compounds of pharmaceutical significance.

Characteristic of the man was his concentration upon the most important and most difficult problems which came to his attention. The easier problems were left to others. He did not know discouragement and by his ability, coupled with persistence, he contributed in a major way to any subject he explored.

Honors came to him from every land. He was awarded the Nobel prize in chemistry in 1915 for his researches on chlorophyll and other plant products; the Davy Medal of the Royal Society of London in 1932; the Willard Gibbs Medal of the Chicago Section of the American Chemical Society in 1933. He was an honorary member of the German, British and American Chemical Societies, and a member of more than a dozen Academies of Science in different countries.

Richard Willstätter was an indefatigable worker and a great teacher who inspired his students and collaborators and kindled their enthusiasm. His stimulation has left a lasting impression on all those fortunate enough to have worked with him.

In spite of the many sorrows that entered his life in the early loss of his wife and only son, and later in the loss of all his possessions and in his forced exile from Germany, his personal troubles did not dim his interest or his leadership in the progress of organic chemistry. His former students owe him much. The world of science is indebted to him for his contributions and mourns the passing of this inspiring and brilliant scientist.

ROGER ADAMS

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Optical Crystallographic Studies with the Polarizing Microscope. V. Ellipsoidal Dispersion in the Picrates of Various Amines

BY J. MITCHELL, JR., AND W. M. D. BRYANT

The systematic application of the various types of dispersion and other optical properties to the identification of amines in the form of their picric acid salts follows directly upon the ground work of dispersion measurement outlined in two preceding papers of this series.[1] The picrates have long been favorite derivatives for the characterization of nitrogen bases through their melting points, but due to the large number of possible derivatives involved, additional more specific physical criteria are desirable. The great sensitivity of optic axial angle and the optical ellipsoid axes to changes in the wave length of light in this series makes ellipsoidal dispersion a powerful and discriminating tool.

The present study covers picric acid and the picrates of thirty-two bases, including ammonia and nineteen lower members of the aliphatic monoamine series; the remaining thirteen are derivatives of polyamines, hydroxylated amines and cyclic bases. Four of the salts occur in two distinct modifications and a fifth occurs in three modifications. The six high temperature forms (designated as II or III) are in each case obtained from the melt. This brings to thirty-nine the number of distinct crystal species covered in this research.

Measurable dispersion of the optic axes was present in all of the compounds studied. Six showed no other type of dispersion. There were thirteen examples of crossed axial plane dispersion, four of axial dispersion with change of sign, three of inclined dispersion, two of horizontal dispersion and fifteen examples of crossed dispersion. Many of the materials exhibited more than one type of dispersion. No examples of triclinic dispersion could be recognized in this group of compounds. Of the substances investigated only picric acid and its ammonium salt appear to have been the subject of earlier optical studies.[2] Attention was given to the "red modification" of ammonium picrate discussed by Davis[3] in order to establish its relationship to the usual yellow form.

Extension of the spectral range of the optical equipment into the near infrared by photographic means proved feasible and this expedient was used to advantage in studying three of the derivatives.

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(1) (a) Bryant, THIS JOURNAL, 63, 511 (1941); (b) Paper IV, *ibid.*, 65, 96 (1943). The term *ellipsoidal dispersion* is used in preference to *selective dispersion* employed in 1a in the same connection.

(2) Groth, "Chemische Krystallographie," W. Engelmann, Berlin, 1917, Vol. IV, pp. 116–119.

(3) Davis, "The Chemistry of Powder and Explosives," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 167–168.

Materials.—The various picrates were prepared directly from J. T. Baker Co. C. P. picric acid (1 mole) and the free bases[4] (1.25 moles). In most cases the base was added directly to a saturated (6%) solution of the acid in 95% ethanol and the crystalline product recrystallized from the same solvent or from a more dilute aqueous alcohol. Some of the picrates were too soluble to be obtained in this way. These were prepared by adding the base to a 1% solution of picric acid in absolute ether. The products were recrystallized from an ether–ethanol mixture (ethanol–water in the case of hydroxyethylethylenediamine and diethylenetriamine picrates). The bases treated in this way were: *n*- and isopropylamine, diethylamine, *n*-butylamine, di-*n*- and di-isopropylamine, diethylaminoethanol, hydroxyethylethylenediamine and diethylenetriamine.

Optical Equipment and Technique.—The main features of both apparatus and procedure were the same as in two preceding papers.[1] However, the following technical refinements are worth mentioning. The strong dispersion encountered in this series required well characterized monochromatic light of good purity covering as much of the spectrum as possible. The General Electric H-4 and S-4 mercury vapor lamps supply up to eight different wave lengths of monochromatic light as indicated in earlier papers.[1b,5] The G. E. H-4 type mercury–cadmium lamp was employed in this research to supplement the ordinary H-4 lamp. The 6438 Å. radiation was isolated by Corning filters 241 (50%, 4.5 mm. thick) and 428 (3 mm. thick), the 5086 Å. line by Wratten 12 and 48, and the 4800 Å. line (with some 4916 Å.) by Jena BG-12 (2 mm. thick) and Corning 338. A combination to isolate the 4678 Å. line was not found, so this line was isolated by means of a Bausch and Lomb monochromator.

To obtain a full selection of monochromatic light for the study of dispersion in interference figures, the monochromator was illuminated by a carbon arc but it proved necessary to adhere closely to the following routine in order to obtain reliable results. The exit slit (shutter eyepiece) was focused so that its outline was clearly visible framing the interference figure. The slit was then closed until only a narrow stripe of monochromatic light was visible down the center of the field. The micrometer eyepiece of the microscope was used with the scale vertical and parallel to the length of the slit. In measuring simple axial or crossed axial plane dispersion the trace of the axial plane was placed along the luminous slit and the points of emergence of the optic axes read on the vertical scale. In determining the wave length of uniaxiality it is essential that the center of the uniaxial cross lie directly on the image of the slit. Crossed dispersion was also measured with the axial plane vertical. Horizontal dispersion was measured with the trace of the axial plane at right angles to the length of the slit. The monochromator was calibrated by means of the mercury spectrum with the exit slit practically closed. Various Corning filters were used to "clean up" the light from the monochromator when working with crystals in their region of strong absorption.

Photographs of interference figures of *n*-propylamine, tri-*n*-propylamine and guanidine picrates in the infrared region were made using the equipment described in paper III[1] for use in the near ultraviolet. The light source consisting of a low voltage ribbon filament tungsten lamp with a Wratten 87 filter, but without a water cell, was not strictly monochromatic although the combination of filter cutoff and a fairly narrow film sensitivity range served to locate the center of the band used with fair precision. Using Eastman infrared film or spectroscopic N-I plates the maximum photographic response should be at 8000 ± 100 Å. provided the sample is non-absorbing. Using spectroscopic Z-I plates hypersensitized with ammonia and the same source the peak of response was less certain but appeared to be above 8600 Å. Infrared film and N-I plates required an exposure of three to eight minutes. With hypersensitized Z-I plates an exposure of twenty to thirty minutes was needed.

The bulk of the refractive indices were determined by the immersion method using interference figures as an aid in selecting the correct orientations and adhering to the practice of saturating the immersion liquid with the crystals and restandardizing wherever solubility was appreciable. In those cases where a refractive index could not readily be measured because of a persistently unfavorable crystal habit, or in the one instance of a γ index too high to be matched by available immersion liquids, the universal stage was employed and the sample embedded in a standard liquid roughly half way between a known refractive index and the one sought. Where the calculated birefringence was not too high, plate II from part I of Winchell's "Elements of Optical Mineralogy"[6] was used. In other cases it was necessary to employ the graphical extrapolation method of Wood and Ayliffe[7] but where this method is used with the universal stage a correction for refraction of the glass hemisphere must also be applied. Some idea of its magnitude may be obtained by extrapolating the correction curves given by Winchell. For example, γ for guanidine picrate is calculated to be 2.195 uncorrected. The correction by extrapolation amounts to about -0.011, hence the final value of 2.184, or 2.18 when rounded off.

The birefringence, $\gamma - \beta$, of picric acid and its dispersion were measured by the new precise "method of lens crystals" described by E. E. Jelley[8] using a fused quartz plano-convex lens of 8 cm. radius.[9] The technique was modified so that the diameters of the interference rings could be read visually on a linear ocular-micrometer scale. Also Newton rings were obtained by reflection instead of transmission, using a plane unsilvered mirror placed below the objective at a 45° angle.[10] The 5461 Å. line of mercury was used for calibration instead of sodium light. Dispersion measurements were obtained by the successive use of different wave lengths of monochromatic light, since a microspectrograph was not available.

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[4] Except the guanidine salt which was obtained from the carbonate.

[5] Bryant, THIS JOURNAL, **55**, 3201 (1933); *Am. Mineral.*, **20**, 281 (1935).

[6] Winchell, "Elements of Optical Mineralogy," 5th ed., Part I, John Wiley and Sons, Inc., New York, N. Y., 1937.

[7] Wood and Ayliffe, *Phil. Mag.*, [7] **21**, 324 (1936).

[8] Jelley, *Ind. Eng. Chem., Anal. Ed.*, **13**, 196 (1941).

[9] Obtained from the Torrisi Laboratories, 4828 N. 13th Street, Philadelphia, Pennsylvania.

[10] The authors are grateful to Dr. Jelley for suggesting this expedient and also for other suggestions contributing to the successful application of his method.

Table I

Dispersion of Optic Axes in Amine Picrates

Picrate	Optic axial angle 2 H_a in degrees (wave lengths in parentheses)						
Monomethylamine	38(6908)	42(6234)	47.5(5780)	53(5461)	72(4800)		
Monoethylamine	29.5(7600)	30.5(7500)	34(6908)	44.5(5780)	50(5461)	65(4916)	70(4850)
Triethylamine	20(6908)	20.5(6234)	21.5(5780)	22(5461)	25.5(5086)	28.5(4700)	28.5(4650)
Diethylaminoethanol (II)	31.5(6908)	32.5(6438)	33.5(5780)	34.5(5461)	37(5086)	38.5(4916)	40(4800)
Di-*s*-butylamine	67.5(6908)	69(6438)	71.5(5780)	72(5461)	74.5(5086)	78.5(4916)	
Diisobutylamine (I)	35(6908)	38(6438)	46(5780)	52(5461)	64(5086)	75.5(4916)	91(4800)

Dispersion and Other Optical Data

Picric Acid.—This substance shows only relatively weak dispersion. The optic axial angle results are as follows: 2 H_a = 102° (4358), 101° (4750), 98.5° (5000, 5461), 98° (5780), 97.5° (6234), 97° (6908) (*vide* Fig. 1); 2 H_0 = 111° (4358), 115.5° (5461, 5780), 118° (6908). The dispersions of 2 H_a and 2 H_0 are therefore consistent and do not show the "inversion" effect reported by Brugnatelli.[11] His 2 H_a values are 1.5° higher than the authors', hence are in fair agreement, but his 2 H_0 results show the wrong trend and the datum for 5893 Å. is almost certainly too high by about four degrees. The birefringences $\gamma - \beta$ for various wave lengths are as follows: $\gamma - \beta$ = 0.0347 (4358), 0.0385 (5461), 0.0389 (5780), 0.0394 (6348), 0.0406 (6908), all ± 0.0005. The result by the "lens crystal" method agrees with $\gamma - \beta$ = 0.038 (5461) calculated from the refractive indices in Table V. Crystals presenting Bx_0 are elongated || γ (confirmed by etch figures).

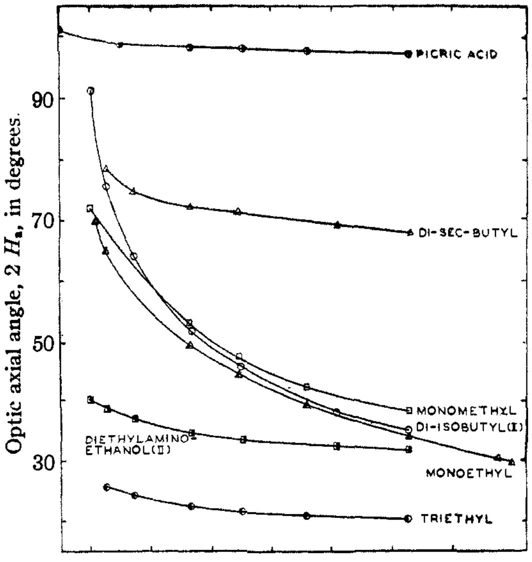

Fig. 1.—Dispersion of optic axes in amine picrates.

Axial Dispersion in Amine Picrates.—Salts having no appreciable dispersion other than that of the optic axes are included in Table I. This effect is considerable, however, and curves like those in Fig. 1 may be utilized for identification. Diisobutylamine picrate (I) may have axial dispersion with change of sign as indicated by the rapid increase in 2 H_a at the shorter wave lengths.

Crossed Axial Plane Dispersion.—Examples of this property are numerous among the picrate salts as may be seen from Fig. 2 and Table II. Infrared photography was required in completing the dispersion curves of the guanidine (*vide* photographs, Fig. 3) and tri-*n*-propylamine salts, for without the infrared measurements it would not have been certain that the axial planes were crossed in these instances.

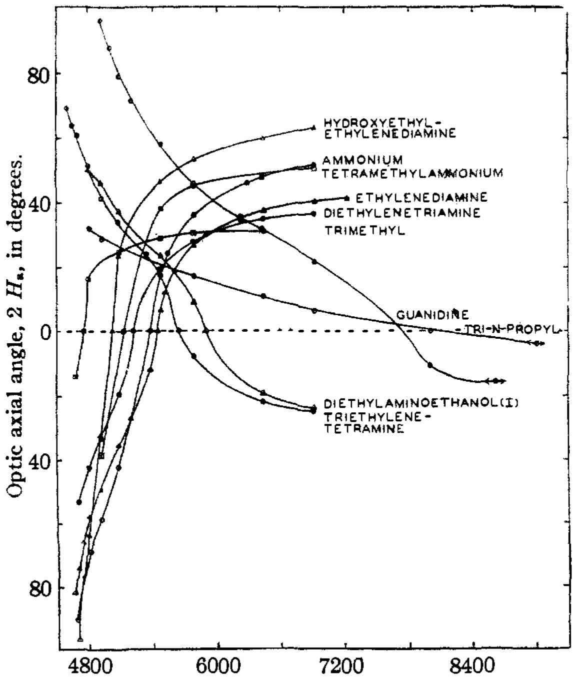

Fig. 2.—Crossed axial plane dispersion in amine picrates.

In most cases the crystallographic faces corresponding to the axial planes were unknown so

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[11] Brugnatelli, *Z. Krist.*, **24**, 274 (1895).

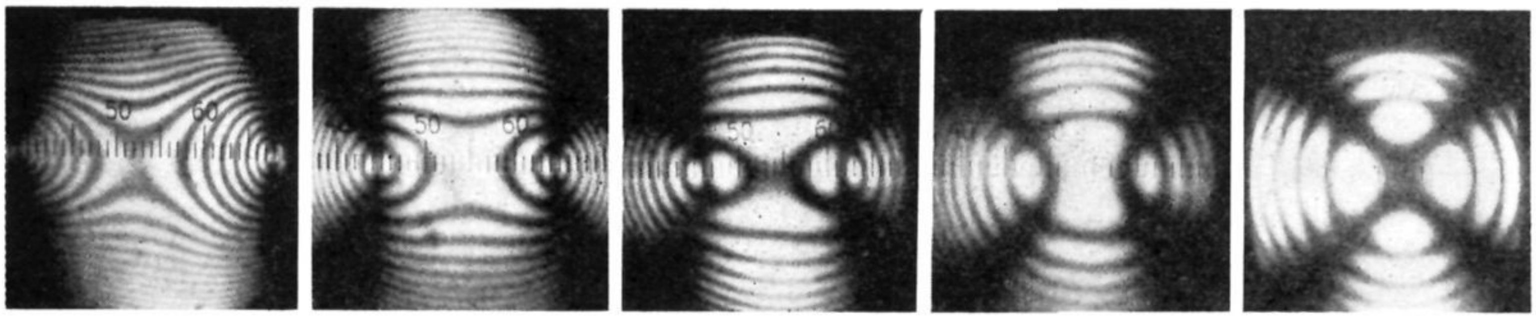
TABLE II

CROSSED AXIAL PLANE DISPERSION IN AMINE PICRATES

Picrate	Wave length of uniaxiality, Å.	Optic axial angle, 2 H_a in degrees							
		λ = 6908	6438	5780	5461	5086	4916	4800	Other wave lengths
Ammonium (yellow)	5380 ± 20	51.5	48	36	17.5	*42	*59	*71	46(6234); *90(4678)
Ammonium ("red")	5380 20	53.5	51.5	35.5	16.5	*43.5	*60.5	..	
Trimethylamine	4670 20	..	31	30.5	29	24.5	..	16.5	*14(4678)
Tetramethylammonium	5120 30	51	47.5	45.5	38	..	*38.5	..	
Di-*n*-propylamine	4840 10	38.5	38.5	37.5	35	28	18	..	
Tri-*n*-propylamine	~8000	*6.5	*11	*16.5	*18.5	*24	*28.5	..	4(>8600); 0(8000); *31.5(4820)
Guanidine	~7750	*21.5	*31.5	*47.5	*58	*79	*96	..	16(>8600); 10.5(*ca.* 8000); *71.5(5200); *78.5(5100); *88(5000)
Ethylenediamine	5435 ± 20	40.5	37	26.5	6.5	*35.5	*49	*58	29.5(5893); 19(5600); 12(5500); *12(5380); *27.5(5200); *66.5 (4750); *74(4700); *82(4650)
Diethylenetriamine	5210 20	36.5	35	28	20	*19.5	*33	*42	*53(4700)
Hydroxyethylethylenediamine	5025 20	63	60	53.5	46.5	23.5	*32.5	*63.5	*76.5(4750); *97(4700)
Triethylenetetramine	5645 10	24.5	22	8	*17.5	*34	*41.5	*51	*24(5340); *61(4700); *64(4650); *69(4600)
Diethylaminoethanol	5900 20	23.5	19	*9	*24	*37.5	*46.5	*50.5	

* Indicates plane of optic axes differs by 90° from its position for extreme red radiation.

the scheme of plotting used in Fig. 2 is somewhat arbitrary. Crossed axial plane dispersion accompanies other types of dispersion in the picrates of dimethylamine (axial dispersion with change of sign) and di-*n*-propylamine (inclined dispersion) and probably also in the hexamethylenetetramine derivative (inclined dispersion).



5200 5780 6234 6908 *ca.* 8000

Fig. 3.—Interference figures of guanidine picrate in monochromatic light (crossed axial plane dispersion in the near infrared); wave length of light in Å.

Ammonium Picrate ("Red Modification").—This salt was obtained in orange-red crystals by the method recommended by Davis.[8] Optical examination indicates that this material is not a distinct polymorph as in the case of thallous picrate discussed by Groth,[12] but instead is a slightly contaminated form of the yellow ammonium salt showing essentially the same crystal habit and only minor differences in optical properties (*vide* Table II). The pleochroism is of the same type as that of the yellow salt but the color along β is deeper and more of a red tint, indicating an oriented inclusion of a more highly colored substance, possibly picramide, in the crystal lattice.

Axial Dispersion with Change of Sign.—The present group of salts contains three (or possibly four) examples of this obscure type of dispersion, described in detail apparently for the first time in the preceding paper. *Dimethylamine picrate* is optically neutral at 4820 ± 20 Å., optically positive above and negative below this wave length, and in addition is uniaxial at 4620 ± 5 Å. The birefringence, $\gamma - \beta$, exhibits a maximum at 5400 ± 40 Å. detectable by the change in motion of the isochromatic curves as the wave length of light is varied. Since neither bisectrix is perma-

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[12] Groth, "Chemische Krystallographie," Vol. IV, p. 79.

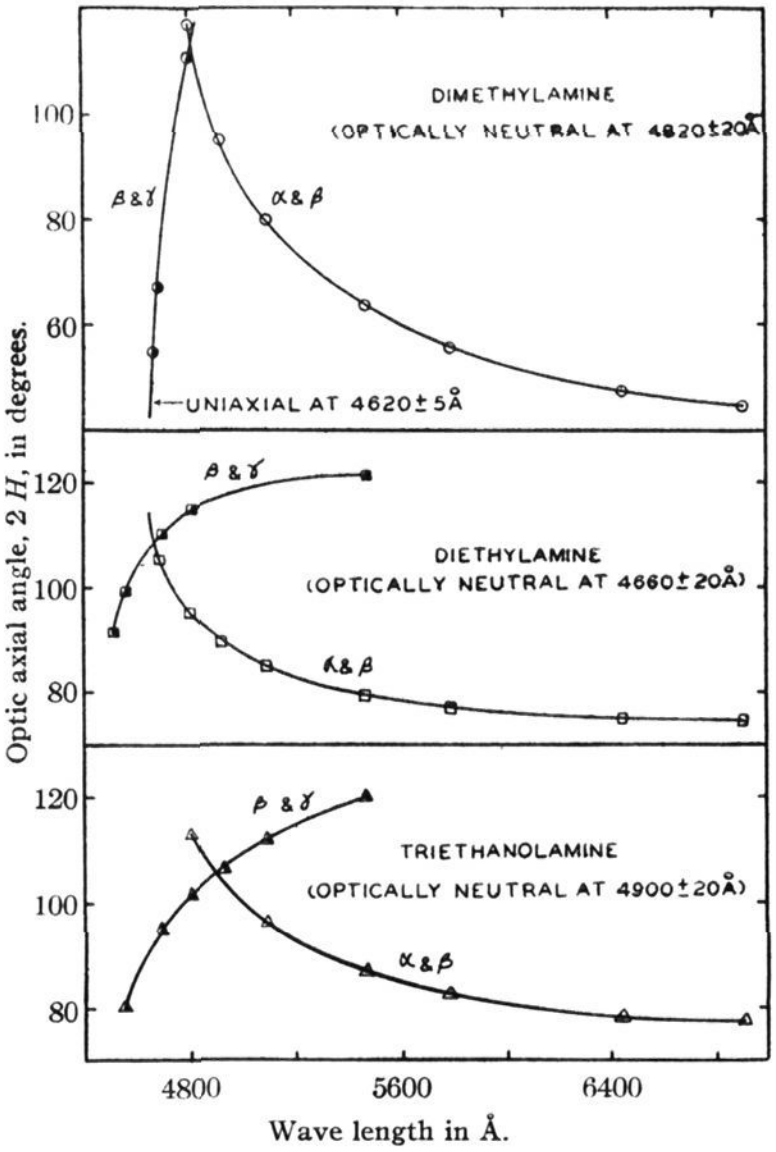
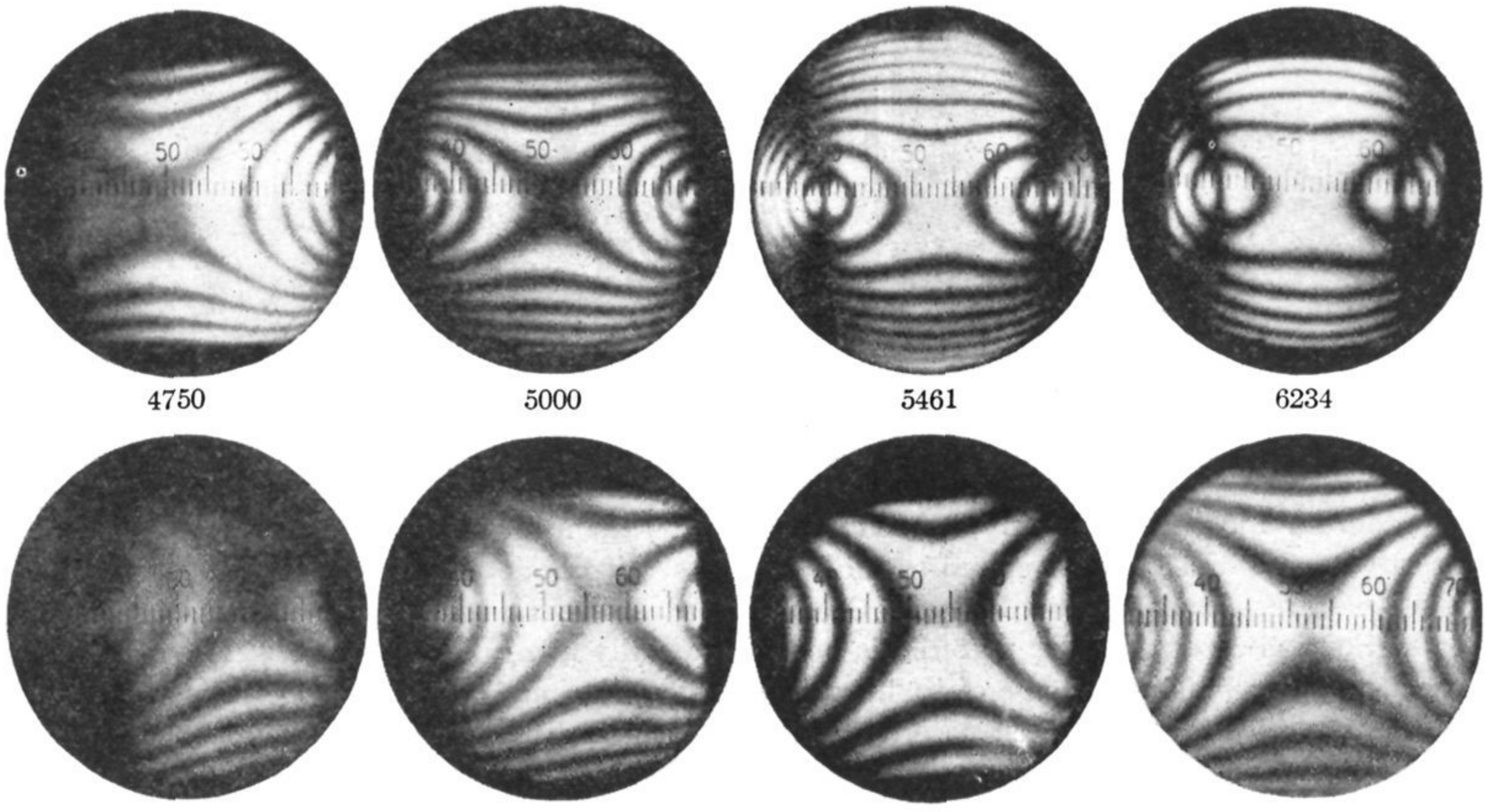


Fig. 4.—Axial dispersion with change of sign in amine picrates.

nently either acute or obtuse, each must be identified by the refractive index with which it coincides. The optic axial angle data are as follows: $2\,H\ (Bx = \gamma) = \sim 117°$ (4800), 95° (4916), 80° (5086), 63° (5461), 55.5° (5780), 47.5° (6438) and 44° (6908). $2\,H\ (Bx = \alpha) = \sim$ *96° (4490), $\sim$ *73° (4520), $\sim$ *45° (4560), $\sim$ *31° (4595), $\sim$ *18° (4610), 0° (4620), 15° (4630), 38.5° (4640), 55° (4660), 67° (4678), 111° (4800). These values are plotted at the top of Fig. 4, and Fig. 5 shows photographs of the interference figures.

Diethylamine picrate becomes optically neutral at 4660 ± 20 Å., is positive above and negative below this wave length. There is a maximum in $\gamma - \beta$ at 4900 ± 20 Å. $2\,H\ (Bx = \gamma) = 105.5°$ (4678), 94.5° (4800), 89.5° (4916), 84.5° (5086), 79° (5461), 77° (5780), 75° (6438) and 74° (6908). $2\,H\ (Bx = \alpha) = 91°$ (4500), 99° (4550), 110° (4678), 115° (4800), 121° (5461) (Fig. 4, center). This salt also exhibits measurable monoclinic crossed dispersion, which assumes the following values for the intervals 6908 Å. $- \lambda$: 0° (6438), 0.5° (5461), 1° (5086), 2° (4916), 2.5° (4800), 3° (4678) and 5° (4550).

Triethanolamine picrate is optically neutral at 4900 ± 20 Å., positive for longer wave lengths and negative for shorter. There is a maximum in $\gamma - \beta$ near 5300 ± 100 Å. and a minimum near



4750 5000 5461 6234

4700 4750 5000 5461

Fig. 5.—Interference figures of dimethylamine picrate in monochromatic light (axial dispersion with change of sign); wave length of light in Å.

4550 Å. 2 H ($Bx = \gamma$) = ~ 113° (4800), 96° (5086), 86.5° (5461), 82.5° (5780), 78° (6438) and 77.5° (6908). 2 H ($B\dot{x} = \alpha$) = 80° (4540), 95° (4678), 101° (4800), ~106° (1496), 111.5° (5086), ~ 120° (5461) (Fig. 4, bottom). There is appreciable crossed dispersion with (6908 − λ) = 0° (6438), 0.5° (5780), 1° (5461), 4° (5086), 6.5° (4916), 9° (4800), 14° (4678).

Diisobutylamine picrate (I) discussed earlier may have this type of dispersion. Strong absorption has obscured the relations between Bx_a and Bx_o and prevented an experimental verification.

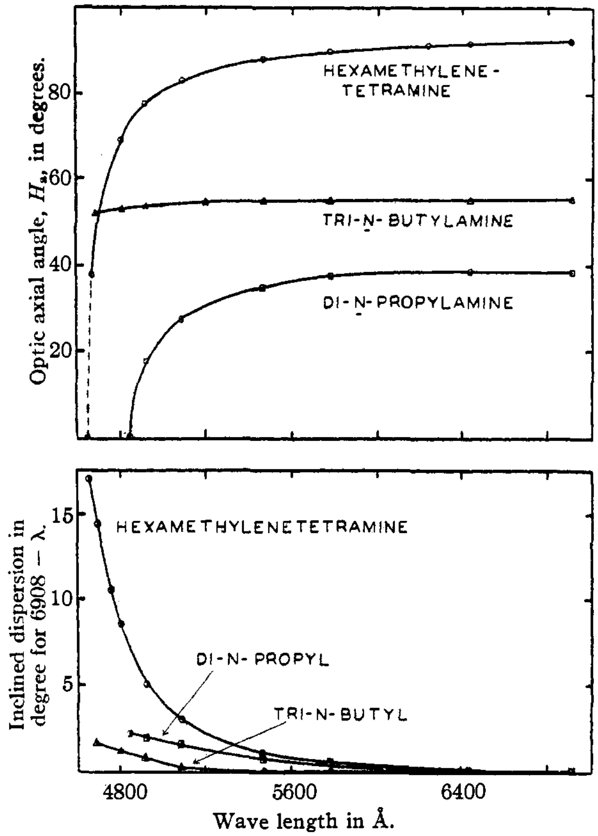


Fig. 6.—Inclined dispersion in amine picrates (apparent values relative to cedar oil, n = 1.515).

Inclined Dispersion.—Three compounds of the group have inclined dispersion (Fig. 6). *Hexamethylenetetramine picrate* is outstanding in this respect. The dispersion is to a large extent confined to one optic axis and does not become appreciable until the green is reached on passing to shorter wave lengths. The optic axial angle and dispersion of this substance are as follows

λ, ±10 Å.	2 H_a	Apparent inclined dispersion 6908 − λ
6908	92.5 ± 1°	0°
6438	91.5	0
6234	91	..
5780	90	0.5
5461	88	1
5086	83	3
4916	78	5
4800	69	8.5
4750	..	10.5
4678	38	14.5
4650	~ 0	~17

Crossed axial plane dispersion is probably present also but due to strong absorption this could not be established beyond question. Di-n-propylamine picrate has moderate inclined dispersion and crossed axial plane dispersion

λ, ±10 Å.	2 H_a	Apparent inclined dispersion 6908 − λ
6908	38.5°	0°
6438	38.5	0
5780	37.5	0.5
5461	35	.7
5086	28	1.6
4916	18	1.8
4840	0	2.2

Tri-n-butylamine picrate, the third example, shows very little dispersion of any kind until the region of absorption is approached

λ	2 H_a	Apparent inclined dispersion 6908 − λ
6908 6438		
5780 5461	55°	0°
5086	54.5	0.2
4916	53.5	.8
4800	53	1.2
4678	52.5	1.7

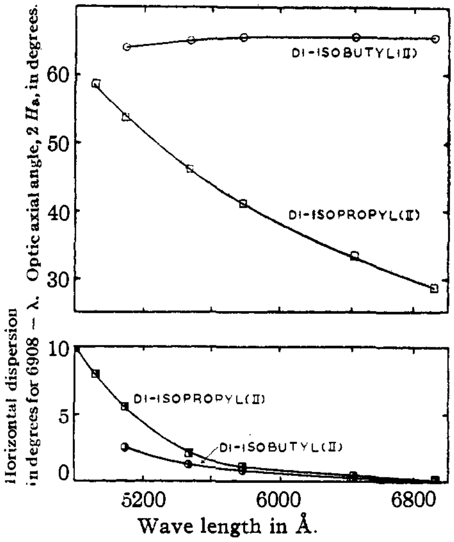
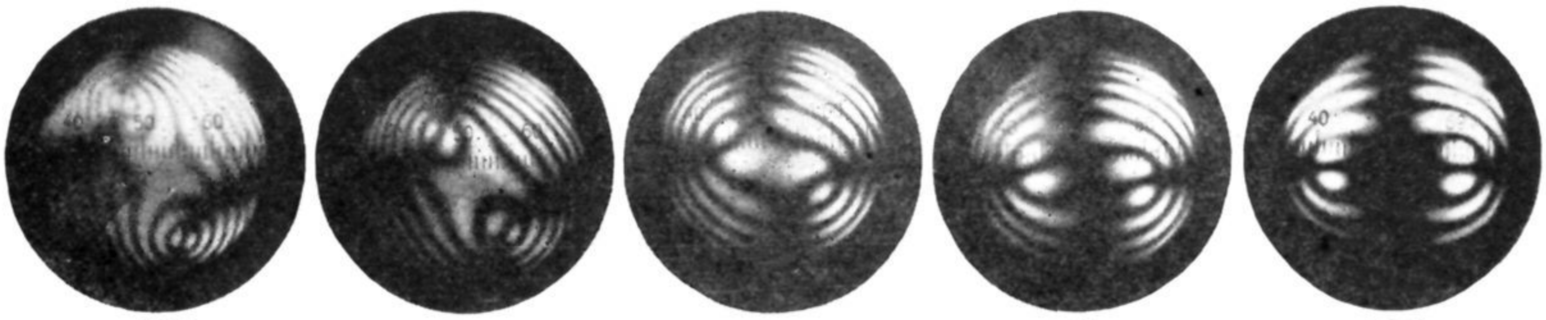


Fig. 7.—Horizontal dispersion in amine picrates (apparent values relative to cedar oil. n = 1.515).



4750 4916 5200 5461 6234

Fig. 8.—Interference figures of *n*-propylamine picrate in monochromatic light (crossed dispersion).

Horizontal Dispersion.—This type of dispersion occurs less frequently than many of the others. However, there are two examples among this group of salts (Figure 7). *Diisopropylamine picrate* (II) has fairly strong horizontal dispersion

λ	$2\ H_a$	Apparent horizontal dispersion 6908 − λ
6908	28.5°	0°
6438	33.5	0.5
5780	41	1
5461	46	2
5086	53.5	5.5
4916	58.5	8
4800	..	10

Diisobutylamine picrate (II) has moderate horizontal dispersion but very little axial dispersion

λ	$2\ H_a$	Apparent horizontal dispersion 6908 − λ
6908	65.5°	0°
6438	65.5	0.2
5780	65.5	.7
5461	65	1.1
5086	64	2.6

Crossed Dispersion.—More of the picrates studied in this research have the above type of dispersion than any other. (Fig. 8 shows photographs of interference figures.) The property is easily measured and is frequently accompanied by other distinctive optical phenomena. Table III contains the optic axial angle data. Inspection of Fig. 9 shows that distinct minima are present in most of the $2\ H_a$ curves. The wave lengths of these minima are useful subcriteria of identity. Minima in the birefringence curves of the Bx_a section frequently but not invariably accompany minima in $2\ H_a$. The high temperature form of *pyridine picrate* appears to exhibit a slight maximum in $2\ H_a$ but in this case the crossed dispersion is not great. The crossed dispersion values for this group are summarized in Table IV and Fig. 10.

Other Optical and Crystallographic Properties.—The principal refractive indices α, β and γ for the entire group of compounds are given in Table V. These data were measured at 25 ± 3° using the monochromatic green radiation (5461 Å.) from the mercury arc. The birefringences, $\gamma - \alpha$, are included for purposes of comparison.

Table III

Axial Dispersion Accompanying Crossed Dispersion in Amine Picrates

Picrate	Optic axial angle $2\ H_a$ in degrees							
	λ = 6908	6438	5780	5461	5086	4916	4800	Other wave lengths
n-Propylamine	47	45	40	35	..	37	46	50(>8600); 49.5(8000); 30(5165); 50(4750); 56.5(4700)
Isopropylamine	44	30.5	25.5	28.5	44	53.5	62.5	25(5850); 73(4678)
n-Butylamine	54.5	54	49.5	46.0	39	..	27	23.5(4830); 37(4700); 46(4650)
Isobutylamine	47.5	44.5	38.5	31.5	29	..	46	26(5220); 26.5(5200); 31(5000); 38(4900); 61(4700)
Diethanolamine	59	57	50.5	45.5	33	25	32	28(4900); 44(4700); 45(4600)
Diisopropylamine (I)	51.5	51.5	52	53	56	58.5	..	50.5(7200)
Tetraethylammonium	51	52	59.5	66	88	..	..	73(5300); 81(5200)
Di-*n*-butylamine	65	63	60.5	58	..	..	44	37(4700); 32.5(4600); 36(4550); 44(4500)
Morpholine (I)	58	57	54.5	52	44.5	37	27.5	26(4780); 26.5(4750); 32(4700); 38(4670); 41(4650); 46(4600)
Morpholine (II)	45.5	44	41	40.5	43.5	51	57	40.5(5500); 41(5300); 71(4650)
Piperazine	64.5	64	61	60.5	55	53	49.5	49(4750); 49.5(4700); 53(4600); 62.5(4500); 69.5(4450)
Pyridine (I)	**69.5**	**68.5**	**65.5**	**64**	**62**	**64.5**	**71**	
Pyridine (II)	**74.5**	**75**	**75**	**76**	**76**	**75.5**	**74.5**	**74(4700)**

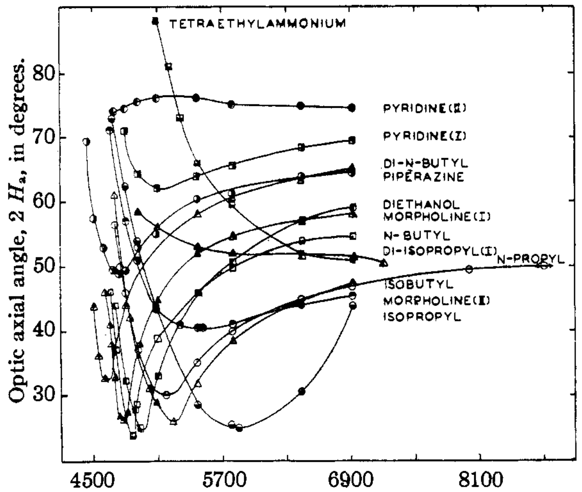


Fig. 9.—Dispersion of optic axes accompanying crossed dispersion in amine picrates.

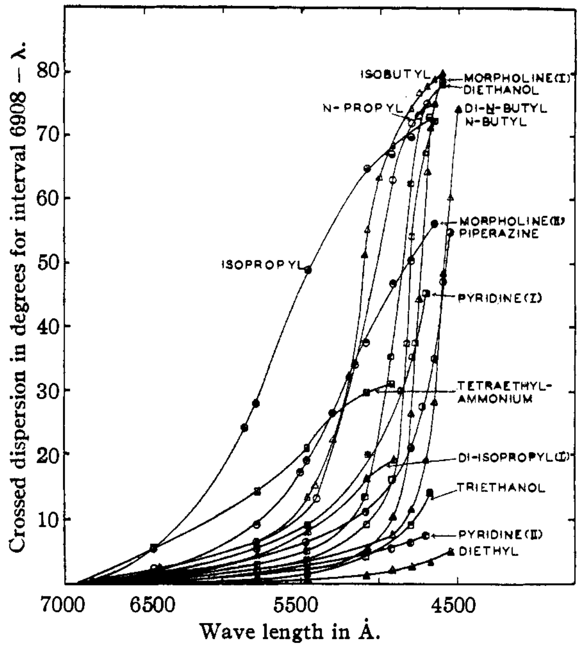


Fig. 10.—Crossed dispersion in amine picrates.

The consistency of α, β and γ for each compound was verified by calculating 2 V from them and comparing the result with 2 V calculated from 2 H_a and β. The elongations of the various substances were observed but these are not tabulated since this property is too sensitive to preparative details to be considered critical. Extinction in sections perpendicular to Bx_a and Bx_o was noted instead. This is parallel or symmetrical in almost all cases except where there is crossed dispersion. In all the salts listed in Table IV extinction is oblique for the Bx_a section, the particular angle varying with the wave length. The same is true of the Bx_o section in diethylamine and triethanolamine picrates. There is apparent oblique extinction in Bx_a sections of the dimethylamine and tri-*n*-propylamine salts, but the position of etch figures and striae indicate parallel extinction.

The crystal systems of picric acid[13] and a few of the above picrates[14] are known but a majority of the salts has not been studied. From the optical properties and general symmetry considerations all but one crystal species (diisobutylamine picrate (III) is uniaxial negative, hence either

TABLE IV

CROSSED DISPERSION IN AMINE PICRATES

Picrate	Crossed dispersion in degrees for the interval 6908 − λ						
	λ = 6438	5780	5461	5086	4916	4800	Other wave lengths
n-Propylamine	2	6	13	..	63	72	34(5165); 73(4750); 75(4700)
Isopropylamine	5	28	49	65	67	69	24(5850); 73(4678)
n-Butylamine	0	1	3	9	..	54	37(4830); 67(4700); 72(4650)
Isobutylamine	2	6	13	55	68	74	15(5400); 22(5300); 32(5200); 51(5100); 63(5000); 77(4750); 78(4700); 79(4650); 80(4600)
Diethanolamine	.	2.5	4.5	13	..	62	35(4920); 75(4700); 78(4600)
Diisopropylamine (I)	1	4	8	16	19	..	
Tetraethylammonium	5	14	21	30	31	..	
Di-*n*-butylamine	1	2	3	5	7	11	4(5200); 6(5000); 9(4850); 19(4700); 28(4650); 48(4600); 60(4550); 74(4500)
Morpholine (I)	0	1.5	2	5	10	26	42(4760); 44(4750); 64(4700); 71(4670): 75(4650); 79(4600)
Morpholine (II)	2	9	19	37	47	50	17(5500); 26(5300); 56(5640)
Piperazine	0	3	6	11	16	21	28(4750); 35(4700); 47(4600); 55(4550)
Pyridine (I)	1	5	9	20	30	35	37(4780); 45(4695)
Pyridine (II)	0	1	2	3	5	6	7(4700)

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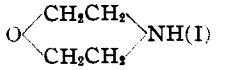
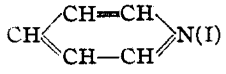
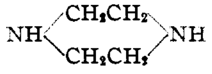
[13] *Z. Krist.* Strukturbericht, Vol. II, 1928–1932, p. 896.

[14] Groth, "Chem. Krystallographie," Vol. IV, pp. 78–80, 116–125.

TABLE V

OPTICAL CONSTANTS OF AMINE PICRATES IN MONOCHROMATIC LIGHT (5461 Å.)

Picrate	M. p. °C. (cor.)	Refractive indices[a]			Birefringence γ − α, and opt. char.	2 V (calcd.)	
		α	β	γ		2 H_a & β	α, β & γ
CH_3NH_2	211	1.473	1.878	1.987	0.514 −	42°	44°
$(CH_3)_2NH$	160	1.648	1.689	1.855	.207 +	56	57
$(CH_3)_3N$	213.5	1.457	1.790	1.815	.358 −	24	26
$C_2H_5NH_2$	170	1.447	1.900	1.994	.547 −	40	39
$(C_2H_5)_2NH$	74	1.558	1.640	1.825	.267 +	72	73
$(C_2H_5)_3N$	173	1.467	1.735	1.745	.278 −	19	19
n-$C_3H_7NH_2$	138	1.455	1.790	1.828	.373 −	30	32
i-$C_3H_7NH_2$	150	1.451	1.806	1.831	.380 −	24	25
(*n*-$C_3H_7)_2NH$	97.5	1.478	1.751	1.781	.203 −	30	32
(*i*-$C_3H_7)_2NH(I)$	147.5	1.476	1.759	1.833	.357 −	45	47
(*n*-$C_3H_7)_3N$	115.5	1.455	1.674	1.677	.222 −	17	16
n-$C_4H_9NH_2$	145.5	1.455	1.753	1.810	.355 −	40	41
i-$C_4H_9NH_2$	151	1.470	1.821	1.848	.378 −	26	27
(*n*-$C_4H_9)_2NH$	64.5	1.480	1.680	1.743	.263 −	52	53
(*i*-$C_4H_9)_2NH(I)$	119	1.510	1.770	1.829	.319 −	44	45
(*s*-$C_4H_9)_2NH$	111	1.474	1.711	1.827	.353 −	62	61
(*n*-$C_4H_9)_3N$	107	1.473	1.641	1.690	.217 −	51	52
$(CH_3)_4N^+$	>300d	1.450	1.789	1.822	.372 −	32	31
$(C_2H_5)_4N^+$	261.5	1.525	1.774	1.868	.343 −	56	56
$(CH_2NH_2)_2$	246–248d	1.470	1.916	1.919[b] (calcd.)	.449 −	5	..
$NH(C_2H_4NH_2)_2$	225–227d	1.480	1.858	1.871	.391 −	16	18
$C_2H_4(NHC_2H_4NH_2)_2$	247–248d	1.505	1.865	1.872	.367 −	14	13
$(CH_2)_6N_4$	187–189d	1.621[d]	1.822	1.948	.327 −	71	69
$(HOC_2H_4)_2NH$	110	1.518	1.787	1.833	.315 −	38	40
$(HOC_2H_4)_3N$	128	1.575	1.651	1.783	.208 +	80	79
$(C_2H_5)_2NC_2H_4OH(I)$	79	1.465[d]	1.793	1.807	.342 −	20	20
$HOC_2H_4NHC_2H_4NH_2$	224–227d	1.575	1.837	1.879	.304 −	38	39
$NH{=}C(NH_2)_2$	315d	1.422	1.998	2.18[d] ± 0.01	.76 −	44	44
 $O\langle\genfrac{}{}{0pt}{}{CH_2CH_2}{CH_2CH_2}\rangle NH(I)$	151.6	1.504[d]	1.852	1.926	.422 −	42	42
 $CH\langle\genfrac{}{}{0pt}{}{CH{=}CH}{CH{-}CH}\rangle N(I)$	167–168	1.549	1.893 ±0.005	1.997[d] ±0.005	.448 −	50	49
 $NH\langle\genfrac{}{}{0pt}{}{CH_2CH_2}{CH_2CH_2}\rangle NH$	>300d	1.526	1.832 ±0.005	1.913	.387 −	50	48
NH_4^+	239–241d	1.515	1.926	1.934	.419 −	14	13
H^+ (picric acid)	121.9	1.680[d]	1.709	1.747	.067 +	84	84[c]

[a] Corrected to 25 ± 3°; precision ± 0.003 except where noted. [b] Calculated from α, β and 2 V. [c] Same value from 2 H_a and 2 H_o; 83° from 2 H_o and β. [d] Measured on universal stage.

tetragonal or hexagonal) appear to belong to the orthorhombic or monoclinic systems. The orthorhombic is excluded where inclined, horizontal or crossed dispersion is present. Axial, crossed axial plane and *axial dispersion with change of sign* may be associated with either system.

Summary

1. The optic axial angle 2 *H* and dispersion of picric acid and a group of thirty-two picrates of amines have been measured in monochromatic light from 6908 Å. in the red to the limit of transmission in the blue.

2. The group is increased to thirty-nine crystal species due to polymorphism and includes thirteen examples of *crossed axial plane dispersion,* fifteen of *crossed dispersion,* three of *inclined dispersion,* two of *horizontal dispersion,* and at least three examples of the obscure *axial dispersion with change of sign.*

3. The principal refractive indices, α, β and γ, and other optical properties of all of the low temperature species have been determined for the green mercury radiation (5461 Å.). These properties together with the optic axial angle and dispersion data constitute a precise means of identifying the parent amines.

4. The optic axial angles of *n*-propylamine,

tri-*n*-propylamine and guanidine picrates were measured photographically in the near infrared using ordinary microscope and camera equipment.

5. Red ammonium picrate is evidently not a distinct polymorph but simply a slightly contaminated form of the yellow salt. The optical properties and crystal habit of the two materials are not significantly different.

WILMINGTON, DELAWARE RECEIVED JULY 6, 1942

[CONTRIBUTION NO. 459 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Kinetics of the Reaction between Ascorbic Acid and Oxygen in the Presence of Copper Ion

BY ETHEL SILVERBLATT,[1] A. L. ROBINSON AND C. G. KING

The oxidation of ascorbic acid (vitamin C) by molecular oxygen is catalyzed with remarkable activity by copper ion. Many fundamental aspects of the reaction have not been clarified in reasonable degree, however. Among recent papers, the studies of Schummer,[1a] Dekker and Dickinson[2] and Hand and Greisen[3] are especially pertinent to the present investigation.

The reaction is of interest, too, because the most active and widespread natural catalysts for the same reaction in plants are formed reversibly from copper ion and protein.[4,5,6]

The present paper deals with (a) qualitative and quantitative evidence for the formation of hydrogen peroxide in the oxidation, (b) correlations between the total oxygen consumption and the production of hydrogen peroxide and dehydroascorbic acid, and (c) the kinetics and mechanism of the first oxidative step.

Procedure

Manometric Studies.—A Warburg respirometer with Pyrex glassware was used for the determination of oxygen consumption. All water used for crystallization of reagents or preparing solutions was triply distilled from Pyrex stills, the last distillation being from a conductivity type (Yoe) still. The vitamin solution, 0.3 ml., was placed in the side-arm of the Warburg vessels. Phosphate buffer was used to adjust the *p*H of the solutions above 4; sulfuric acid was added for the lower range. 5.35×10^{-5} *M* copper sulfate and 6.6×10^{-3} *M* ascorbic acid were studied over a *p*H range of 6.3 to 3.0. The reaction was stopped by the addition of 3 ml. of 4% metaphosphoric acid. The solution was washed into an Erlenmeyer flask with 2% metaphosphoric acid and titrated at once with 2,6-dichlorobenzenone-indophenol as described by Bessey and King.[7] After a short initial period, the oxidation of ascorbic acid invariably consumed oxygen in excess of that required for conversion to dehydroascorbic acid. The excess increased with decreasing *p*H values, indicating that dehydroascorbic acid was being oxidized further or that a significant amount of hydrogen peroxide was being formed.

Recoveries of 96 to 100% of the ascorbic acid were obtained regularly by hydrogen sulfide reduction after oxidation by either oxygen or iodine, showing that the oxidation was not proceeding appreciably beyond the dehydroascorbic acid stage.

The presence of "active oxygen" was demonstrated by (a) the release of iodine from potassium iodide, (b) oxidation of Fe^{++} to Fe^{+++} ion, and (c) a modification of these two effects by the addition of catalase. The addition of 0.1 ml. of purified liver catalase solution quickly destroyed the capacity of the solutions to give positive tests for the oxidation of either I$^-$ or Fe^{++}. Tests in Warburg vessels, comparing excess oxygen uptake with the oxygen liberated by catalase, and checked against the liberation of iodine from I$^-$, gave values in close agreement, considering the small quantities and techniques involved (*e. g.*, 5.19 ± 0.75 cu. mm. of oxygen liberated, against 5.65 cu. mm. calculated from the titration). We believe that these results justify acceptance of the postulate that hydrogen peroxide is formed in the catalytic oxidation of ascorbic acid, and that it is relatively stable under the conditions of the experiment.

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[1] The present paper is based upon a thesis presented by one of the authors (E. S.) to the Graduate School of the University of Pittsburgh, June, 1940.

[1a] Schummer, *Biochem. Z.*, **304**, 1 (1940).

[2] Dekker and Dickinson, THIS JOURNAL, **62**, 2165 (1940).

[3] Hand and Greisen, *ibid.*, **64**, 358 (1942).

[4] McCarthy, Green and King., *J. Biol. Chem.*, **128**, 455 (1939).

[5] Stotz, *Proc. Am. Soc. Biol. Chem.*, **9**, c (1940).

[6] Lovett-Janison and Nelson, THIS JOURNAL, **62**, 1409 (1940).

[7] Bessey and King, *J. Biol. Chem.*, **103**, 698 (1933).