

LXIX.—*On the Correspondence between the Magnetic Rotation and the Refraction and Dispersion of Light by Compounds containing Nitrogen.*

By J. H. GLADSTONE, Ph.D., F.R.S., and W. H. PERKIN, Ph.D., F.R.S.

The substances containing nitrogen, the magnetic rotation of which was described in Dr. Perkin's recent paper, have been examined by Dr. Gladstone with reference to their refraction and dispersion. The following table contains the refractive indices calculated from the observations.

Liquid Substances.

	Temp.	Sp. gr.	μ_A .	μ_F .	μ_H .
Propylamine	6.5°	0.7329	1.3922	1.4022	1.4111
Dipropylamine	4.4	0.7530	1.4066	1.4191	1.4281
Tripropylamine	4.4	0.7703	1.4197	1.4306	1.4408
Isobutylamine	6.8	0.7437	1.3999	1.4099	1.4188
Diisobutylamine	7.6	0.7546	1.4109	1.4211	1.4301
Allylamine	5.2	0.7787	1.4234	1.4377	1.4502
Methyl-aniline	7.8	0.9983	1.5640	1.5966	1.6324
Dimethylaniline	8.2	0.9675	1.5514	1.5834	1.6198
Pentamethylenediamine	17.5	0.8821	1.4577	1.4699	1.4803
Piperidine	7.0	0.8753	1.4542	1.4661	1.4757
Pyridine	12.2	0.9875	1.5037	1.5254	1.5468
Propionitrile	20.0	0.7843	1.3636	1.3723	1.3792
Trimethylene cyanide	24.2	0.9858	1.4315	1.4420	1.4506
Methyl nitrate	19.8	1.2090	1.3703	1.3809	1.3908
Ethyl „	20.4	1.1078	1.3805	1.3912	1.4005
Propyl „	19.6	1.0569	1.3931	1.4036	1.4134
Isobutyl „	18.8	1.0165	1.3991	1.4099	1.4193
Nitroglycol	18.5	1.4910	1.4417	1.4550	1.4671
Nitroglycerin	18.6	1.5942	1.4682	1.4818	1.4945
Nitromethane	17.5	1.1394	1.3782	1.3898	1.4009
Nitroethane	20.5	1.0489	1.3875	1.3983	1.4090
Nitropropane	22.7	1.0022	1.3954	1.4063	1.4164
Isobutyl nitrite	24.2	0.8638	1.3682	1.3784	1.3888
Chloropierin	17.5	1.6623	1.4577	1.4708	1.4829

In addition to these liquids, the refraction was determined of several gaseous, liquid, or solid bodies dissolved in water, namely, ethylamine, ethylamine hydrochloride, diethylamine hydrochloride, triethylamine hydrochloride, piperidine hydrochloride, hydriodic acid, ammonium iodide, ammonium nitrate, and ammonium sulphate. In each case the solution was a very strong one, so that the probable error from necessary dilution of the substance was never great.

The following table contains the molecular magnetic rotation, molecular refraction, and the molecular dispersion of the substances in question, together with those of a few others where the three properties have not been determined from the same specimen; the latter are indicated by *.

Substance.	Formula.	Mol. mag. rotation.	Molecular refraction.	Molecular dispersion.
*Ammonia	NH ₃	1·810	9·03	0·50
*Ethylamine	NEtH ₂	3·609	24·47	1·19
*Diethylamine	NEt ₂ H	5·662	39·36	1·96
*Triethylamine	NEt ₃	8·518	54·62	2·76
Propylamine	NPrH ₂	4·563	31·57	1·52
Dipropylamine	NPr ₂ H	7·549	54·80	2·62
Tripropylamine	NPr ₃	11·664	77·91	3·92
Isobutylamine	NBuH ₂	5·692	39·25	1·86
Diisobutylamine	NBu ₂ H	9·936	70·24	3·29
*Ammonium chloride	NH ₃ ·HCl	6·096	22·33	1·52
Ethylamine hydrochloride ..	NEtH ₂ ·HCl ..	7·997	37·18	2·06
Diethylamine „	NEt ₂ H·HCl ..	9·896	51·86	2·69
Triethylamine „	NEt ₃ ·HCl	11·724	65·78	3·26
Tetraethylammonium chloride	NEt ₄ Cl	13·626	80·70	3·78
Allylamine	NAlH ₂	5·587	30·99	1·96
*Aniline	NC ₆ H ₇	16·162	52·09	5·96
Methylaniline	NC ₆ H ₆ Me	19·629	60·45	7·33
Dimethylaniline	NC ₆ H ₅ Me ₂	22·823	68·96	8·55
Pentamethylene diamine	(NH ₂) ₂ (CH ₂) ₅ ..	7·492	52·93	2·61
Piperidine	NC ₅ H ₁₁	5·810	44·11	2·09
„ hydrochloride	NC ₅ H ₁₁ ·HCl ..	10·034	56·57	2·96
Pyridine	NC ₅ H ₅	8·761	40·30	3·44
Propionitrile	NC ₃ H ₅	3·331	25·50	1·09
Trimethylene cyanide	(NC) ₂ (CH ₂) ₃ ..	5·136	41·15	1·82
Methyl nitrate	MeNO ₃	2·057	23·59	1·30
Ethyl „	EtNO ₃	3·084	31·26	1·64
Propyl „	PrNO ₃	4·085	39·05	2·02
Isobutyl „	BuNO ₃	5·180	46·72	2·36
Nitroglycol	C ₂ H ₄ (NO ₂) ₂ ..	3·768	45·08	2·59
Nitroglycerin	C ₃ H ₅ (NO ₂) ₃ ..	5·405	66·67	3·74
Nitromethane	MeNO ₂	1·858	20·25	1·22
Nitroethane	EtNO ₂	2·837	27·71	1·53
Nitropropane	PrNO ₂	3·819	35·11	1·87
Isobutyl nitrite	BuNO ₂	5·510	43·90	2·35†
Chloropierin	CCl ₃ NO ₂	5·384	45·29	2·50
Hydrochloric acid (36·5 p. c.)	HCl	4·215	14·45	1·12
Hydriodic acid (65·1 p. c.) ..	HI	17·868	31·87	4·19
Hydrobromic acid (dilute) ..	HBr	8·533	20·65	2·19
Ammonium iodide	NH ₃ ·HI	19·878	39·66	4·88†
*Nitric acid	HNO ₃	1·180	16·50	1·13
*Sulphuric acid	H ₂ SO ₄	2·315	22·37	0·97
Ammonium nitrate	NH ₃ ·HNO ₃ ..	2·316	25·23	1·88
„ sulphate	(NH ₃) ₂ H ₂ SO ₄ ..	4·980	39·50	1·78

† Estimated from μ_F and μ_G .

‡ Estimated from μ_F .

752 CORRESPONDENCE BETWEEN MAGNETIC ROTATION, ETC.,

The object of this table is to draw attention to the general correspondence that exists between these three different properties of the substances in question; a correspondence that points to some connection between the rotation of the polarised ray under magnetic influence and the retardation of the rays of light in passing through a material substance.

The three columns, though expressing different properties, are really comparable with one another, for in each case the observed value is divided by the density of the substance, and it is determined not for equal weights but for an equal number of molecules. This is shown by the formulæ employed for reducing the observations.

Molecular magnetic rotation = $\frac{r \times Mw}{r' \times Mw' \times d}$, where r , Mw , and d

represent respectively the observed rotation, molecular weight, and density of the substance, and r' and Mw' the corresponding values for water. Molecular refraction, generally called refraction equivalent,

= $Mw \frac{\mu_A - 1}{d}$, and molecular dispersion, or dispersion equivalent, =

$Mw \frac{\mu_H - \mu_A}{d}$, where μ_A and μ_H are the refractive indices of the lines A

and H of the solar spectrum. It has been found that each property is determined in the first instance by the atomic composition of the substance, so that it may be laid down as a primary law that the molecular magnetic rotation, refraction, or dispersion of a compound is the sum of the molecular magnetic rotation, refraction, or dispersion of its constituents. The values which have been deduced under this primary law, mainly from the paraffin-group, are, however, subject to large modifications, dependent upon differences in the structure of the compound. Thus a change of valency is attended by a marked change of value in these optical properties, and they are apparently affected by some circumstances which are not as yet recognised in our structural formulæ.

From the primary law above given, the following values have been deduced by Perkin for the molecular rotation of certain elements in the paraffin-group of carbon-compounds, and against them have been placed the normal values for their molecular refraction and dispersion arrived at by Landolt, Brühl, and Gladstone.

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
CH ₂	1·023	7·6	0·34
C	0·515	5·0	0·26
H	0·254	1·3	0·04
O, alcoholic	0·194	2·8	0·10
O, aldehydic	0·261	3·4	0·18
Cl	1·733	9·9	0·50
Br	3·562	15·3	1·22
I	7·757	24·5	2·62
N, in amines	0·717	5·1	0·38

A glance at this table will show that the three columns are quite independent. The relative figures for one substance do not correspond with those for another, although there is a certain analogy between them.

Directly, however, that we turn to the modifications that are introduced by changes in the mode of combination, we find that when a change occurs in the one property it is noticeable also in the other two, and these changes are in the same direction, though not to the same extent; in fact, the variations in the magnetic rotation are usually greater than those in the dispersion, and these again are much more marked than in the refraction.

This was first observed by us some years ago. It struck us as a remarkable coincidence that the separate investigations showed two different values for oxygen in alcohols and aldehydes, and that there was a very great exaltation of the values in the case of unsaturated carbon-compounds, such as those containing allyl. We observed also that the value of CH₂ in the first and second member of the homologous series (such as the alcohols, the fatty acids, &c.) was different from its value in the higher members of the same series, and that these differences were always in the same direction. We have since noticed also that where there was an abnormally large molecular rotation, as in methylene iodide, there is an abnormally large molecular refraction and dispersion.

Nor have we been the only observers who have been aware of some connection between the two sets of phenomena. H. Becquerel, in his "Experimental Researches on Magnetic Rotatory Polarisation," printed in the *Ann. Chem. Phys.*, of 1877, drew up a table, which showed a certain rough relationship between that property and the refractive index. But as he took no account of differences in density or molecular weight, he failed to recognise the connection between these and chemical constitution.

754 CORRESPONDENCE BETWEEN MAGNETIC ROTATION, ETC.,

Kanonnikoff (*J. Russ. Chem. Soc.*, 1888) also has pointed out some curious relations between the specific rotatory and the refractive power of those chemical substances which under ordinary circumstances exhibit circular polarisation. But this kind of rotation appears to be a totally different phenomenon from that produced by exposure in a magnetic field.

The series of compounds containing nitrogen seem to afford a remarkably good opportunity for comparisons, and the results have exceeded our expectations. We propose now to consider only the more salient points, leaving the smaller questions for future consideration.

I. *Compound Ammonias*.—At the commencement of the second table will be found two good series of compound ammonias, the one resulting from the successive substitution of ethyl for hydrogen, and the other from successive substitution of propyl. The difference for the first is C_2H_4 , and for the second C_3H_6 , and the value of these groups is found by subtracting the figures for ammonia from those for ethylamine, ethylamine from diethylamine, &c. In every instance there is an increase, and these are given by the following table:—

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
Ethyl, 1st substitution	1·799	15·44	0·69
„ 2nd „	2·053	14·89	0·77
„ 3rd „	2·856	15·26	0·80
Normal increase for C_2H_4	2·046	15·2	0·68
Propyl, 1st substitution	2·753	22·54	1·02
„ 2nd „	2·986	23·23	1·10
„ 3rd „	4·115	23·11	1·30
Normal increase for C_3H_6	3·069	22·8	1·02

A noteworthy fact here is the rapid augmentation of the molecular rotation for each additional C_2H_4 or C_3H_6 . The same is clearly indicated also in the molecular dispersion. It is doubtful in the molecular refraction, but the irregularities of the numbers are such as may be due to experimental error.

II. *Hydrochlorides of the Compound Ammonias*.—The increase for each addition of C_2H_4 in this series is as follows, starting from ammonia hydrochloride:—

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
Ethyl, 1st substitution.....	1·901	14·85	0·54
„ 2nd „	1·899	14·68	0·63
„ 3rd „	1·828	13·92	0·57
„ 4th „	1·902	14·92	0·52
Normal increase for C_2H_4	2·046	15·2	0·68

The numbers were obtained from the examination of these salts in aqueous solution.

In this series, unlike the preceding, there is no progression in the increase, the additional amounts remaining about the same in regard to the rotation, refraction, and dispersion. There is also another point of correspondence between the three optical properties. In the case of each of them the increase never amounts to the theoretical quantity.

III. *Compound Anilines*.—The short series of methylanilines gives the following increases for each addition of CH_2 , starting from aniline.

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
1st substitution.....	3·467	8·36	1·37
2nd „	3·194	8·51	1·22
Normal increase for CH_2	1·023	7·6	0·34

Here the increase in the molecular rotation for each CH_2 is more than three times that which is usually observed in a series belonging to the paraffin group. An equally large augmentation is manifest in the molecular dispersion, and a very visible increase occurs in the refraction. This exaltation of the dispersion equivalent of CH_2 in some members of the aromatic group was observed by Gladstone and Dale as far back as 1866.

IV. *Unsaturated Carbon Compounds*.—The table includes three very different examples of unsaturated carbon compounds, allylamine, pyridine, and aniline with its substitution compounds. In each case the observed value is considerably greater than that which would be calculated from the normal values for carbon, hydrogen, and ammonia in the paraffin series.

756 CORRESPONDENCE BETWEEN MAGNETIC ROTATION, ETC.,

	Molecular magnetic rotation.		Molecular refraction.		Molecular dispersion.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
Allylamine.....	5·587	4·040	30·99	29·23	1·96	1·44
Pyridine.....	8·761	4·562	40·30	36·63	3·44	1·88
Aniline.....	16·162	5·585	52·09	44·23	5·96	2·22

It will be observed not only that there is a great increase in each case, but that whilst in allylamine, where there is only one pair of double-linked carbon atoms, the increase is considerable, in aniline, where there are three such pairs, the increase in rotation and dispersion is about seven times as much, and in refraction the increase is more than four times as great.

V. *Nitriles compared with Ammonias*.—It was observed many years ago that the refraction equivalent of nitrogen in nitriles and cyanides was smaller than in the nitrogen bases, and this observation was recently extended to the dispersion equivalent. The second table affords two opportunities of testing this in regard to the molecular magnetic rotation, namely, propionitril and trimethylene cyanide. By subtracting the normal values for hydrogen and carbon from the observed values for these compounds we obtain the values of nitrogen.

Nitrogen.	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
From amines.....	0·717	4·9	0·38
„ propionitrile.....	0·516	4·0	0·11
„ trimethylene cyanide.....	0·518	4·2	0·14

VI. *Nitric Ether Series*.—There is a good homologous series in the second table, commencing with methyl nitrate. Assuming nitric acid to be the first member of the series, we obtain the following values for each addition of CH_2 .

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
1st addition	0·877	7·1	0·17
2nd „	1·027	7·67	0·34
3rd „	1·001	7·79	0·38
4th „ (Isobutyl)	1·095	7·67	0·34
Normal increase	1·023	7·6	0·34

Here there are two points of correspondence to be specially noted. It is evident that neither in the magnetic rotation, refraction, nor dispersion does the first addition of CH_2 produce the normal increase; but whilst this normal increase is found in each of the successive additions, they are all practically alike, and there is no continuous augmentation of the increase as in the case of the compound ammonias. An exception to this last remark is, however, the increase in molecular rotation (1·095) observable in isobutylic nitrate. This, like the iso-compounds in general, is somewhat higher than the normal value, a difference not perceptible in the refraction and dispersion.

VII. *Isobutyl Nitrite and Nitrate*.—Though there are several NO_2 compounds in the table, there is only one true nitrite, that of isobutyl. In his paper, Dr. Perkin has drawn especial attention to the fact, that though this substance contains an atom of oxygen less than the isobutyl nitrate, it has a greater molecular magnetic rotation. This is attributed to the fact that the nitrogen is saturated in one case and not saturated in the other. The difference between the two is shown below for each of the optical properties.

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
Isobutyl nitrite	5·510	43·90	2·35
„ nitrate	5·180	46·72	2·36
Difference for O	−0·330	+2·82	+0·01
Normal difference	+0·261	+3·4	+0·18

Whilst the addition of oxygen has caused an actual diminution in the magnetic rotation, it has given only a doubtful increase in the dispersion and an increase on the refraction considerably below the normal for aldehydic oxygen. The three results, though apparently different, are in the same direction.

758 CORRESPONDENCE BETWEEN MAGNETIC ROTATION, ETC.

The nitro-compounds themselves differ from one another to the usual extent in regard to all three optical properties.

VIII. *Acids and their Ammonium Salts.*—It was among the earliest observations on refraction equivalents that the halogen acids in solution gave abnormal figures, far higher than those deducible from the compounds of the halogens with organic radicals. The same is now shown to hold good for their molecular magnetic rotation. It is also found that these values increase with the dilution of the acid up to a certain extent; and in the following tables the higher values are used. The calculated values for the magnetic rotations are for the *free* acids (see p. 739).

	Molecular magnetic rotation.		Molecular refraction.		Molecular dispersion.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
Hydrochloric acid	4·412	2·187	14·45	11·2	1·12	0·54
Hydrobromic acid	8·533	4·016	20·65	16·6	2·19	1·26
Hydriodic acid ..	18·435	8·211	31·87	25·8	4·19	2·66

Dr. Perkin has shown that these acids in combining with ammonia or piperidine retain their abnormal values, and combine with but little condensation. How far this is true for the other optical properties is shown in the following table. The calculated numbers are the values of the base and acid added together.

	Molecular magnetic rotation.		Molecular refraction.		Molecular dispersion.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
NH ₃ + HCl	6·096	6·230	22·33	23·48	1·52	1·62
NH ₃ + HBr.	10·177	10·351	28·53	29·68	2·49	2·69
NH ₃ + HI.	19·996	20·253	39·66	40·90	4·88	4·69
Piperidine + HCl	10·034	10·222	56·43	58·56	2·96	3·21
Triethylamine } + HCl }	11·739	12·930	65·78	69·07	3·26	3·88

The correspondence is again seen in these cases, and all the three optical properties indicate that although there is but little condensation in the case of ammonia and hydrochloric, hydrobromic, or hydriodic acid, yet there is considerable condensation in the case of the triethylamine-compound with hydrochloric acid.

IX. *Hydrochloric Acid in Solution*.—Although hydrochloric acid, when dissolved in water, has a far greater effect on light than could have been expected, it has recently been found that when dissolved in isoamyl oxide it rotates the plane of polarisation to very little more than the theoretical extent. On examining the refraction and dispersion, a still closer agreement with theory became manifest.

Hydrochloric acid.	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
In water.....	4·412	14·45	1·12
In isoamyloxiide.....	2·238	11·36	0·51
By calculation for free acid	2·187	11·2	0·54

These nine cases of comparison all represent different kinds of departure from what we consider the normal values. They have shown a very marked correspondence between the three optical properties of the substances examined. They have also revealed differences in detail, and it is only fair to add that other peculiarities in the molecular magnetic rotation exist which are not represented by similar peculiarities in the refraction and dispersion. But these exceptions are of such a limited character that on a re-examination of the matter with fresh specimens, and with varied conditions, it is quite conceivable that they may disappear.

It may therefore be laid down as generally, if not always, true, that where there is a departure from the normal values in regard to one or other of these properties, it is to be found in the other two. The different properties are evidently similarly affected by change in chemical constitution. The general drift of the whole comparison appears to us to lead irresistibly to the conclusion that we have here another close relationship between electro-magnetism and the velocity of light.