STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION

Part XXXV. The Rotatory Dispersion of 5-quinolinoimino and amino-camphors (*d* and *dl*)

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The present investigation describes the determination of the rotatory dispersion of the condensation products of 5-aminoquinoline with camphorquinones (*d* and *dl*) and of their reduction products, which are found to exhibit phototropy in chloroform solution.

Nature of the Racemic Modification

The melting points of the racemic forms of 5-quinolino-imino-and-amino-camphor are higher than those of their optical isomers. They are, therefore, true *dl*-compounds. It is further supported as follows. A small amount of the *d*-form was added to the corresponding racemic modification and the melting point was found to be lowered in each case. This clearly shows that the racemic substances are true *dl*-compounds.

Nature of the Rotatory Dispersion

The rotatory dispersion has been determined in the visible region of the spectrum for six wavelengths in the case of the yellow coloured compound, 5-quinolinoimino-*d*-camphor and for twelve wavelengths in the case of the colourless 5-quinolinoamino-*d*-camphor. It is found to be simple, as it obeys the one-term Drude's equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0{}^2}$. In this equation, k_0, the rotation constant may be taken as a measure of the absolute rotation for the wavelength λ for which $\lambda = \sqrt{1 + \lambda_0{}^2}$. The absolute rotation constants (k_0s) are thus numerically but not dimensionally identical with the magnitude of the rotatory powers. Comparisons of rotatory powers and rotation constants at wavelength λ, where $\lambda = \sqrt{1 + \lambda_0{}^2}$, may be regarded as those for corresponding conditions of wavelengths in which the effects of dispersion are eliminated.

THE EFFECT OF SOLVENT ON ROTATORY POWER

The molecular rotatory power, $[M]_D^{32°}$, of the compounds in different solvents is given in Table I. The sequence of their decreasing rotatory power is as follows:—

(*a*) 5-*quinolinoimino*-d-*camphor :*

methyl alcohol > ethyl alcohol > chloroform > acetone = pyridine > benzene.

The sequence agrees with that of the dielectric constants of the solvents except in the case of chloroform and pyridine.

(*b*) 5-*quinolinoamino*-d-*camphor :*

benzene = chloroform > pyridine > acetone > ethyl alcohol > methyl alcohol.

The sequence agrees with that of the dielectric constants in the reverse order except for chloroform.

The above mentioned sequence does not hold good for other wavelengths. For instance for the mercury violet line (Hg 4358), the order of the decreasing rotatory power is

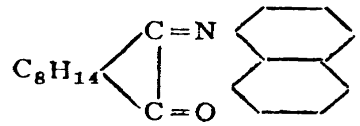
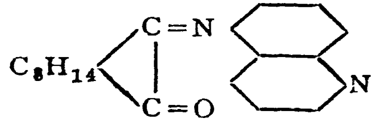
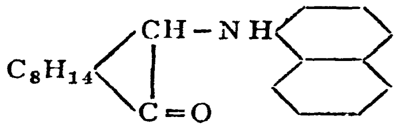
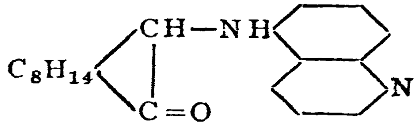
chloroform > benzene > pyridine > acetone > ethyl alcohol > methyl alcohol.

This order is different from that for the sodium D-line. It is, therefore, necessary for any strict comparison of rotatory power of the compounds in a number of solvents that the effects of dispersion should be eliminated. It is not an easy matter when the dispersion is "complex", but when it is 'simple' as in the case of these compounds, which obey the linear relationship, the effects of dispersion can be completely eliminated by using the rotation constants (K_0s) of the Drude's one-term equation as a measure of the absolute rotatory power of the medium. It refers to a wavelength, λ, where $\lambda = \sqrt{1 + \lambda_0^2}$ which is not much greater than 10,000 Å.U. The longest wavelength used in our measurements is 6708 Å.U. (Lithium red) and extrapolation from it to about 10,000 Å.U. is permissible in view of the linear nature of the dispersion equations calculated by us. We have, therefore, included in brackets (Table I) the values of Drude's Molecular Rotation Constants K_0s, as a measure of the absolute rotatory power of the compounds. If we compare these Molecular Rotation Constants (K_0s), the results are somewhat different and the order of the decreasing rotation constants for 5-quinolinoamino-*d*-camphor is as follows:—

ethyl alcohol > pyridine > chloroform = benzene > acetone > methyl alcohol.

TABLE I

$[M]_{D}^{32°}$

No.	Structural Formula	$[M]_{D}^{32°}$					
		Methyl Alcohol (31·2)*	Ethyl Alcohol (25·8)*	Acetone (21·5)*	Pyridine (12·4)*	Chloroform (5·20)*	Benzene (2·28)*
1[c]	 (291)[a]	1425·9 (345·41)[b]	1615·0 (396·05)[b]	1862·4 (446·9)[b]	1734·9 (424·27)[b]	1771·3 (421·8)[b]	1893·2 (437·37)[b]
2	 (292)[a]	1547·6 (376·09)[b]	1518·4 (360·03)[b]	1430·8 (316·82)[b]	1430·8 (316·82)[b]	1460·0 (347·77)[b]	1372·4 (286·40)[b]
3[c]	 (293)[a]	214·24 (52·00)[b]	234·40 (56·34)[b]	266·63 (64·16)[b]	293·00 (67·71)[b]	272·90 (61·17)[b]	293·00 (72·43)[b]
4[c]	 (294)[a]	205·80 (50·680)[b]	213·15 (62·080)[b]	220·50 (54·090)[b]	235·20 (57·150)[b]	249·90 (56·200)[b]	249·9 (56·200)[b]

* It refers to the dielectric constants of the solvents.

(*a*) The values in brackets refer to the molecular weights.

(*b*) The values in brackets refer to molecular rotation constant $\frac{M \times K_0}{100}$.

(*c*) Singh, B. K. and Kapur, N. S., *Proc. Ind. Acad. Sci.*, (A), 1949, **29**, 413.

TABLE II

5-quinolino-imino-d-*camphor*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Conc.	0·400%		0·400%		0·400%		0·400%		0·400%		0·400%	
Calculated $\begin{cases}[\alpha]\\ \lambda_0\end{cases}$	$\frac{128\cdot8}{\lambda^2-0\cdot1041}$ 0·3227		$\frac{123\cdot3}{\lambda^2-0\cdot1121}$ 0·3347		$\frac{108\cdot5}{\lambda^2-0\cdot1258}$ 0·3548		$\frac{108\cdot5}{\lambda^2-0\cdot1258}$ 0·3547		$\frac{119\cdot1}{\lambda^2-0\cdot1092}$ 0·3305		$-\frac{98\cdot79}{\lambda^2-0\cdot1370}$ 0·3701	
Line	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
Li_{6708} ..	372·5	372·5	361·2	362·0	335·6	334·9	335·6	334·9	350·0	349·3	315·7	315·7
Cd_{6438} ..	415·0	415·1	404·4	404·2	375·0	374·9	374·5	374·9	390·0	389·8	355·0	355·9
Li_{6104} ..	478·1	480·0	470·0	469·5	440·0	439·8	439·0	439·8	452·5	452·0	420·0	419·5
Na_{5893} ..	530·0	530·0	520·0	520·0	490·0	490·0	490·0	490·0	500·0	500·0	470·0	470·0
Hg_{5780} ..	560·0	560·6	550·0	551·1	521·2	521·1	521·6	521·1	530·0	529·3	501·9	501·4
Hg_{5461} ..	664·4	664·2	661·5	650·9	629·4	629·6	629·5	629·6	630·0	630·0	612·5	612·2

TABLE III

*5-quinolino-amino-*d*-camphor*

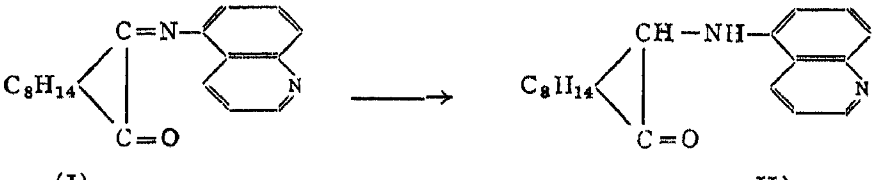
Solvent	Methyl Alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Conc.	0·400%		0·400%		0·400%		0·400%		0·400%		0·400%	
Calculated $\left\{\begin{array}{l}[\alpha]\\ \lambda_0\end{array}\right.$	$\frac{17\cdot24}{\lambda^2-0\cdot1010}$ 0·3178		$\frac{17\cdot92}{\lambda^2-0\cdot1001}$ 0·3164		$\frac{18\cdot14}{\lambda^2-0\cdot1020}$ 0·3194		$\frac{19\cdot78}{\lambda^2-0\cdot1000}$ 0·3162		$\frac{19\cdot32}{\lambda^2-0\cdot1200}$ 0·3464		$\frac{20\cdot87}{\lambda^2-0\cdot1016}$ 0·3187	
Line	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
Li_{6708} ..	49·40	49·40	51·25	51·25	53·02	52·88	56·25	56·53	58·75	58·53	59·37	59·94
Cd_{6438} ..	55·00	54·98	56·87	56·91	58·75	58·86	63·12	62·91	65·58	65·58	66·87	66·73
Li_{6104} ..	63·75	63·62	65·25	65·77	68·12	68·12	73·12	72·67	76·25	76·79	76·87	77·07
Na_{5893} ..	70·00	70·00	72·50	72·50	75·00	75·00	80·00	80·00	85·00	85·00	85·00	85·00
Hg_{5780} ..	73·75	73·96	76·25	76·56	79·37	79·29	84·50	84·50	90·00	90·25	90·00	89·84
Hg_{5461} ..	87·50	87·50	90·62	90·56	93·25	93·00	100·0	100·0	108·1	108·4	106·2	106·3
Ag_{5209} ..	101·0	102·2	104·3	104·7	108·7	108·6	115·6	115·6	127·5	127·7	132·0	123·0
Cd_{5086} ..	109·0	109·3	113·1	113·0	117·5	117·5	125·0	125·0	131·3	131·3	132·5	132·9
Cd_{4800} ..	132·5	132·2	138·1	137·6	143·5	143·4	151·9	151·9	175·0	175·1	162·5	162·2
Cd_{4678} ..	145·6	146·3	150·6	150·9	157·5	157·5	166·2	166·5	195·0	195·4	178·1	177·8
Li_{4603} ..	155·0	155·5	160·0	160·6	167·5	167·5	173·1	176·8	210·6	210·4	189·4	189·4
Hg_{4358} ..	192·5	193·8	199·5	199·5	209·4	209·3	220·0	220·0	276·0	276·3	236·5	236·4

The order, as given above, is different from those for sodium *D*-line (5893 Å.U.) and mercury violet line (4358 Å.U.) and the order of K_0s also does not follow that of the dielectric constants of the solvents.

As already pointed out in our previous work,[1] it will be more rational to compare the rotatory power of the solution with its dielectric constant and not with that of the solvent.

RELATION BETWEEN CHEMICAL CONSTITUTION AND ROTATORY POWER

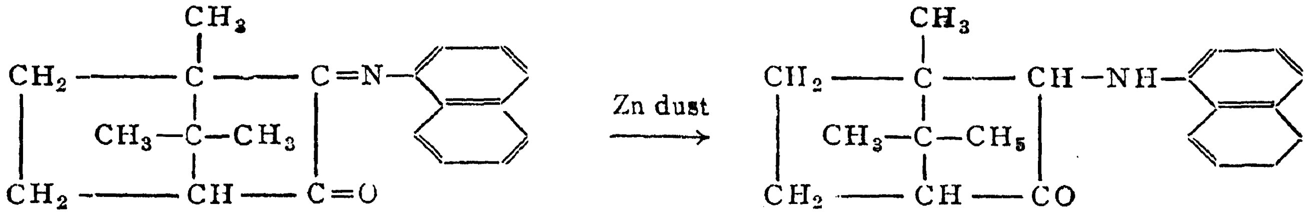
In Table I the molecular rotatory powers, $[M]_D^{32°}$, of four compounds in six solvents are given. It is seen that the rotatory power of the α-naphthylimino-and-amino-*d*-camphor[2] are higher than those of the 5-quinolinoimino-and-amino-*d*-camphor respectively. The molecular weights of the two compounds are almost identical. It is therefore, clear that the quinoline ring has a lower rotatory effect than the naphthalene ring, except in methyl alcohol. This agrees with the previous observations of Singh and Manhas.[3] It is also seen that the reduction of 5-quinolinoimino-*d*-camphor to 5-quinolinoamino-*d*-camphor causes a great fall in the rotatory power owing to the break in the complete conjugation between the double bonds of the carbonyl group, the azethenoid group and the quinoline ring as in the case of α-naphthylimino-*d*-camphor to α-naphthylamino-*d*-camphor (Singh and collaborators)[4] thus:—



(I) (II)

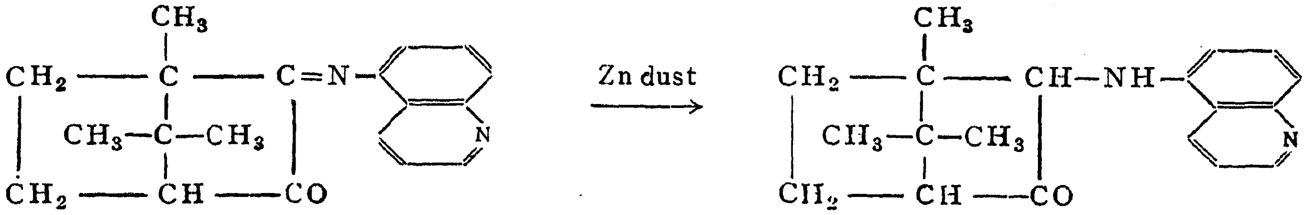
The arylaminocamphors are generally obtained by reduction of the corresponding imino derivatives dissolved in ether, by zinc dust in presence of 10% aqueous potassium hydroxide solution. In the case of 5-quinolinoamino-camphor this method does not yield the pure product as the ethereal solution of the amino-compound, on exposure to the atmosphere, immediately turns deep yellow due to oxidation. The operation was, therefore, carried out in an atmosphere of coal (oil) gas as described in the experimental part. We may recall here the case of *p*-phenylene bisiminocamphor which was prepared by Forster and Thornley[6] but which they failed to reduce to the corresponding amino compound. One of us[7] was however, able to reduce this bisimino derivative to the bisamino stage by avoiding oxidation and isolating the product as the dihydrochloride which was subsequently hydrolysed to the free bisamino compound by water in alcoholic solution.

It may be remarked that although α-naphthyliminocamphor and 5-quinolinoiminocamphor (Formulæ III and IV) are very similar in structure, the product of reduction of the former is not oxidised by oxygen in the atmospheric air. It is thus seen that the nitrogen atom in the quinoline ring has produced this instability; in other words it brings out the fact that the naphthalene ring is more stable than the quinoline ring.



(III)

(Not oxidised by air)



(IV)

(Oxidised by air)

EXPERIMENTAL

5-*Quinolinoiminocamphors* (*d and dl-*).—Equimolecular quantities of camphorquinone (*d* or *dl*) and 5-aminoquinoline were mixed very thoroughly with a sufficient quantity of anhydrous sodium sulphate and were heated in a hard glass boiling test tube fitted with an air condenser on a water-bath for several hours. At times the condenser was removed and the sublimate was pushed down the tube. When the reaction was complete, the product was washed with cold water, filtered and the precipitate was repeatedly recrystallised from aqueous alcohol as yellow prisms.

The compounds are very soluble in methyl and ethyl alcohols and chloroform, less so in acetone and pyridine and insoluble in water.

5-quinolinoimino-*d*-camphor..........m.p. 122-23° C; (N) found 9·48%

5-quinolinoimino-*dl*-camphor........m.p. 153-54° C; (N) found 9·46%

$C_{19}H_{20}N_2O$ requires (N) $= 9{\cdot}58\%$

5-*Quolininoaminocamphor* (*d and dl*).—The ethereal solution of the colourless 5-quinolinoaminocamphor on coming in contact with air gets readily oxidised by turning deep yellow with the result that the product obtained is contaminated. It is thus not possible to obtain in this way the amino compound in the pure form. But, if we carry out the operations in an atmosphere of coal gas, till the final stage, the oxidation can be prevented. We, therefore, carried out the preparation and isolation of the compound in an atmosphere of coal gas; the products thus obtained were pure:—The corresponding imino-derivative was dissolved in ether and 10% aqueous solution of potassium hydroxide and sufficient quantity of zinc dust added. The contents were put in a hard glass stoppered bottle and coal gas was passed into the bottle to displace the air. The bottle was shaken for several hours in an electric shaker till the yellow ethereal layer became colourless. The ethereal layer was rapidly separated, washed with water and ether distilled off. The residue was repeatedly recrystallised from alcohol as colourless needles.

The compounds are soluble in benzene, chloroform, ether, and acetone, less so in methyl alcohol and ethyl alcohol and insoluble in water.

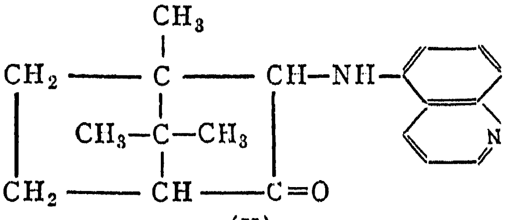
5-quinolinoamino-*d*-camphor, m.p. 132-33 ° C; (N) found 9·26%

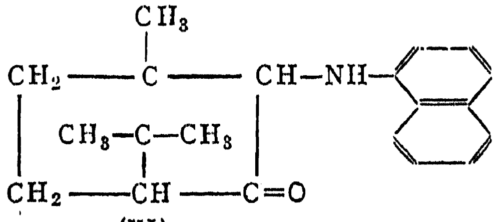
5-quinolinoamino-*dl*-camphor, m.p. 163-64 ° C; (N) found 9·25%

$C_{19}H_{22}N_2O$ requires (N) $= 9 \cdot 52\%$

PHOTOTROPY IN SOLUTION

The phototropic behaviour of α-naphthylaminocamphor (*d*, *l* and *dl*) in chloroform solution as well as in other solvents has been discussed in previous communications by one of us.[5] The structure of 5-quinolinoaminocamphor is very similar to that of the α-naphthyl derivative as shown in formulæ V and VI:


(V)


(VI)

It is found that *d*-and *dl*-forms of the quinoline derivatives exhibit phototropy when their chloroform solutions are exposed to sunlight. The colourless solution turns within a minute or two into bluish green which deepens into deep green with longer exposure. On keeping the coloured solution in dark or even in the ordinary light of the laboratory it turns almost colourless. The colour change is reversible and can be repeated.

We are studying this subject in detail and hope to report further results shortly.

SUMMARY

(1) The rotatory dispersion of 5-quinolinoimino-*d*-camphor and 5-quinolinoamino-*d*-camphor is found in different solvents to obey Drude's one term equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$, it is, therefore, "simple".

(2) The sequence of rotatory power of 5-quinolinoamino-*d*-camphor in different solvents runs in the reverse order of the dielectric constants of the solvents and that in the case of 5-quinolinoimino-*d*-camphor follows the same order of the dielectric constants except with minor discrepencies.

(3) The influence of quinoline and naphthalene ring on the rotatory power has been considered.

(4) The reduction of 5-quinolinoimino-*d*-camphor to 5-quinolinoamino *d*-camphor resulting in a great lowering of its rotatory power, has been discussed.

(5) The nature of the racemic form has also been investigated.

(6) The *d*-and *dl*-forms of 5-quinolinoaminocamphor are found to exhibit phototropy in chloroform solution.

ACKNOWLEDGEMENT

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		Jour. Ind. Chem. Soc., 1930, **7**, 545.
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