

STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XIX. Stereoisomeric Aminoanilino-, and Dimethylaminoanilino-, Methyleneecamphors, and their Derivatives

BY BAWA KARTAR SINGH AND BHUTNATH BHADURI

(From the Departments of Chemistry, University of Allahabad, Allahabad, and Ravenshaw College, Cuttack)

Received November 12, 1941

THE present communication is a continuation of Parts X, XII, XV, XVI and XVII,¹ and consists in the determination of the optical rotatory dispersion of the condensation products of oxymethylenecamphors (*d*, *l*, *dl*) with aminoacetanilides (*o*, *m*, *p*) and with *p*-aminodimethylaniline. The products of hydrolysis of these acetylated compounds afford us an opportunity to study the effect of substitution on rotatory power of a free amino group in the benzene nucleus at different positions.

The condensation product of oxymethylene-*d*-camphor with *o*-aminoacetanilide was an oil which refused to solidify. The *meso* or internally compensated *p*-phenylenebisamino-methyleneecamphor was prepared by condensing *p*-aminoanilino-methylene-*l*-camphor with oxymethylene-*d*-camphor (*vide* Experimental).

p-Aminoanilinomethylene-*d*-camphor was condensed with *d*-camphorquinone in the usual way (*vide* Experimental).

The Effect of Chemical Constitution and the Nature of Solvent on Rotatory Power.—(i) Since polar effect of a substituent group is traceable in optical activity,² we should expect a decrease or increase in the rotation of the derivative according as the substituent group is more negative or positive than the substituted one. The position of NH₂ group in the "polar" series is not known with certainty. Since a parallelism has been drawn between several electrophysical properties such as dissociation constants of substituted acetic or benzoic acids (Rule²), specific inductive capacity (Rule²) and electromagnetic rotation of compounds of the type, C₆H₅X³ and the "polarity" of the substituent group, we can roughly, subject to minor variations, have an idea of the position of the NH₂ and N (CH₃)₂ groups in the "polar" sequence.

For example we get for

Electromagnetic rotation:	$N(CH_3)_2 > NH_2 > Br > OCH_3 > Cl > CH_3 > OH > CHO > CN > COOH > NO_2$;
Specific inductive capacity:	$NO_2 > CN > CO \cdot CH_3 > CHO > Cl > OH > NH_2 > Br > N(CH_3)_2 > OCH_3 > C_2H_5 > CH_3 > H$;
Dissociation constant of $CH_2X \cdot COOH$;	$CN > COOH > Cl > Br > C_6H_5 > H > CH_3 > NH_2 > N(CH_3)_2$;
do. $C_6H_4 X \cdot COOH$;	$NO_2 > COOH > Br > Cl > OH > CH_3 > OCH_3 > H > NH_2 > N(CH_3)_2$.

In these studies, it will be more rational if the effect of substitution on the dissociation constant of the substituted anilines, $C_6H_4X \cdot NH_2$ is compared with the specific rotation of the compounds, which are the condensation products of oxymethylenecamphor with these aromatic bases. The dissociation constant values for these bases give the following sequence:—

Ortho:	$N(CH_3)_2 > H > CH_3 > OCH_3 > Cl > COOH > NO_2$;	} (Landolt)
Meta:	$CH_3 > H > Br > Cl > COOH > NO_2$;	
Para:	$N(CH_3)_2 > OCH_3 > CH_3 > H > Cl > Br > COOH > NO_2$.	

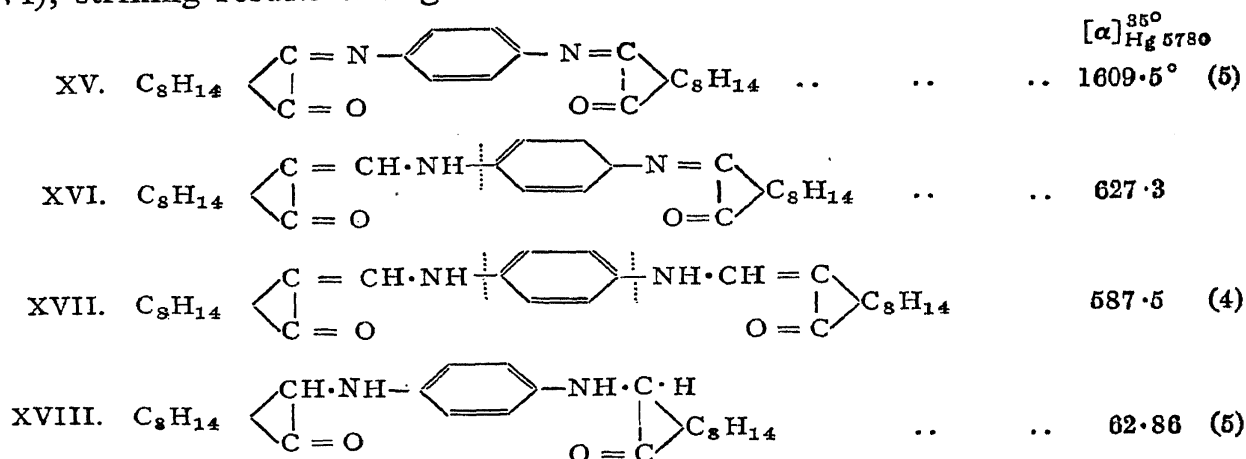
The sequence of rotatory power of *p*-substituted anilinomethylenecamphors in different solvents as revealed by comparing $(\alpha)_{H_g^{5461}}^{35^\circ}$ (Table A), closely corresponds, subject to minor variations, to the Landolt-*p*-series as well as to the different series cited above, representing the influence of substituent groups on specific inductive capacity, electro-magnetic rotation and acidity or basicity of compounds. The analogy between the effect of substitution on optical activity and on other electrophysical properties, which has been previously referred to is, therefore, further confirmed.

The importance of the study of dispersion in the investigations of the effect of constitution on the rotatory power has been repeatedly emphasised by us in previous communications. In our opinion, even this is not sufficient, as we have often come across a number of instances which when compared, lead to diametrically opposite conclusions if we go beyond a certain wave-length and do not confine ourselves to the same for polarimetric examination. (This limit, of course, varies with the nature of the compound and of

the solvent). For compounds which exhibit "simple" dispersion, the solution may be looked for in another direction. In the Drude's equation $[a] = \frac{K_0}{\lambda^2 - \lambda_0^2}$, when $\lambda^2 = \lambda_0^2 + 1$, i.e., for the value of λ always in the *infra-red* region beyond 10,000 Å.U., K_0 is numerically equal to the specific rotation $[a]$ which may be termed the 'absolute rotation' of the compound and which is a constant for the same. This value is independent of the wave-length and it will serve our purpose if we compare the values of K_0 of the different compounds in different solvents with one another. From such a comparison (Table A) for the different *meta*-substituted anilinomethylenecamphors (which have been found without exception to obey the simple dispersion law), we get the sequence, $H > CH_3 > NH_2 > Cl > Br > I$, for all the solvents. Except for the interchanging of the position of Cl and I, this agrees closely with the "polar" series (Rule²): OH^- , Cl, Br, I, NH_2 , C_2H_5 , H^+ , COOH, CHO, $COCH_3$, CN, NO_2 , which represents a gradual transition from highly negative to highly positive polarity.

(ii) *Effect of Acetylation*: Since the introduction of NH_2 group in the benzene nucleus in the *para* position is accompanied by an increase of rotation (Table A), this effect may be expected to be counteracted by the introduction of a strongly positive "acyl" group which introduces an electrostatic moment of opposite orientation to that of the negative NH_2 group. This is in agreement with the observed facts, since experimentally in the *p*-isomerides we get the sequence of decreasing rotatory power as, $NH_2 > Un > NH.Ac$, for all the solvents and for all wave-lengths. But this rule does not hold good in the case of substitution of *m*-isomerides where experimentally we get the sequence: $Un > NH_2 > NH.Ac$, in place of the expected one, $Un > NH.Ac > NH_2$, if not, $NH.Ac > Un > NH_2$: for since the introduction of the NH_2 group in the *meta* position is accompanied by a decrease in rotatory power, the introduction of an *acyl* group may be expected to cause an increase in the rotation of the resulting compound, at least to the extent of being more than that of the amino compound. In previous communications,⁵ we have, however, shown that the acetylation of an amino group generally lowers the rotation of the parent compound; in some cases, so much so, that the sign of the rotatory power is reversed. In the present paper we also observe lowering of rotation on acetylation in general. Hence the assumption that the electric field exerted at the asymmetric atom by the attached side chains is the factor governing optical rotation is either not corroborated by experimental facts or our knowledge of other factors affecting the same is too meagre to explain these deviations accurately and satisfactorily.

(iii) *The Effect of Unsaturated Conjugation* : On comparing the structural formulæ and rotatory power in pyridine of 1 : 4 phenylenebisiminocamphor (XV), 1 : 4 phenylenebisaminocamphor (XVIII), 1 : 4 phenylene bisamino-methylene camphor (XVII) and anilinomethylenecamphor-4-iminocamphor (XVI), striking results emerge:



It is clear that if the conjugation of the azethenoid groups involving the carbon atoms of the terpene nucleus and the nitrogen atoms of the side chain is broken (XV \rightarrow XVIII), depression in rotatory power is phenomenal. The effect is much less marked if the conjugation in the side chain (*i.e.*, outside the terpene nucleus) is broken (XV \rightarrow XVII). In the case of XVI, the conjugation is more complete, if we count from the N = C side—a fact which may account for its slightly higher rotation than that of XVII; in the latter case, the conjugation is broken at both the dotted lines.

(iv) *Position Isomerism and Rotatory Power* : The sequence of the rotatory power of the position isomerides of aminoanilinomethylenecamphors is $p > Un > m$ in all solvents; and for acetylaminoanilinomethylenecamphors, it is $Un > p > m$. This is in partial agreement with the electrostatic modification of Thomson's rule as suggested by Rule,² which predicts for a negative substituent, the rotatory power of the different position isomerides as $p > m > Un > o$.

It is found that the order of decreasing rotatory power in different solvents for all the compounds studied in the present communication is methyl alcohol $>$ ethyl alcohol $>$ acetone $>$ pyridine $>$ chloroform $>$ benzene, for all wave-lengths between $\lambda = 5086$ Å.U. and 6708 Å.U. The sequence of dielectric constants of the solvents is also the same.

From Table A, we also notice that if we compare K_0 , the numerical value of 'absolute rotation,' for the different compounds in different solvents, the sequence of the decreasing values of K_0 is the same as that of their dielectric constants.

Dependence of Optical Rotatory Power on Chemical Constitution 285

These compounds, like other condensation products of bases with oxymethylenecamphor described in previous communications (1, 2, 4, 5, 6) are without exception, found to obey the simple dispersion equation of

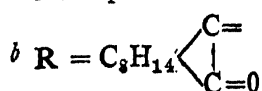
$$\text{Drude, } [\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$$

TABLE A

$$[\alpha]_{\text{Hg}}^{35^\circ}$$

Compound	MeOH	EtOH	Acetone	Pyridine	Chloroform	Benzene
aI. $R^b = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_{11}$	480.0 (86.78) ^c	451.3 (81.83)	448.9 (83.08)	433.2 (81.21)	424.6 (78.57)	367.1 (70.71)
II. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_{10}(\text{CH}_3)$..	454.4 (85.21)	439.9 (81.02)	442.3 (82.31)	405.8 (80.48)	384.8 (68.55)	352.6 (71.37)
III. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_9(\text{CH}_3)_2$..	465.0	440.8	425.8	401.6	401.6	355.4
IV. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_9(\text{Cl})$..	388.5 (63.14)	384.7 (62.47)	388.0 (63.65)	374.4 (63.70)	381.4 (61.22)	363.6 (60.73)
V. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_8(\text{Cl})_2$..	417.7	406.3	401.8	394.4	374.6	359.4
VI. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_7(\text{Br})$..	361.1	355.6	360.6	348.8	324.3	291.9
VII. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_6(\text{Br})_2$ (..)	354.0 (63.49)	348.4 (64.66)	334.3 (59.17)	324.1 (56.74)	279.3 (54.50)
III. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_5(\text{I})$..	338.1 (58.99)	325.9 (54.25)	326.5 (55.22)	318.4 (54.92)	300.0 (54.46)	258.6 (47.82)
IX. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_4(\text{I})_2$..	328.5 (60.38)	319.5 (58.49)	309.7 (57.57)	294.8 (53.64)	279.1 (51.12)	251.1 (47.59)
X. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_4(\text{NH}_2)_2$..	484.8	475.1	461.8	..	428.8	..
CI. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_3(\text{NH}_2)_3$..	437.4 (75.32)	407.2 (73.30)	406.8 (73.55)	393.1 (68.45)	349.3 (60.16)
II. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_2(\text{N}(\text{CH}_3)_2)_2$ (..)	455.9 (71.60)	450.9 (71.45)	420.1 (..)	420.0 (..)	.. (..)
II. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}_2(\text{NH} \cdot \text{COCH}_3)_2$..	385.0 (69.10)	371.7 (66.65)	357.4 (63.81)	353.8 (62.81)	350.3 (58.32)
V. $R = \text{CH} \cdot \text{NH} - \text{C}_6\text{H}(\text{NH} \cdot \text{COCH}_3)_5$..	408.8 (66.60)	400.6 (67.83)	389.9 (67.27)	384.7 (62.97)	377.5 (..)	.. (..)

^a For optical data for compounds I–IX, see reference (1).



^c Figures within brackets refer to the numerical value of K_0 of the Drude equation, $[\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$ referred on page 283 of the theoretical portion, i.e., for λ , when $\lambda = \sqrt{\lambda_0^2 + 1}$.

Physical Identity of Isomers

The values of rotatory power of *d*- and *l*- forms in different solvents (Tables I-V) are identical within limits of experimental error. Out of 136 observations now recorded, in as many as 128 cases, the difference in the numerical value of the specific rotatory power of the opposite isomers corresponds to a difference of less than 0.01° in the observed angle of rotation and in the remaining 8 cases, the corresponding angle lies between 0.01° and 0.02° , which is the limit of experimental error allowable in such measurements. This further supports Pasteur's principle of molecular dissymmetry, according to which the two forms, *dextro* and *laevo*, must possess equal and opposite rotatory power.

The melting point of the racemic form of *m*-acetylamino-anilinomethylenecamphor is higher than that of the optically active isomers. This form is a true *dl*-compound, at least, in the solid state.

Examples of racemic forms having identical melting points with those of the active forms are very rare. A few examples have already been cited in previous communications (^{1, 5, 6}). In the present paper, we record four more similar instances, viz., *p*-acetylaminoanilinomethylenecamphors, m.p. 226-27°; aminoanilinomethylenecamphors:—*meta*, m.p. 64-65°, and *para*, 163-64° respectively and *p*-dimethylamino-anilinomethylenecamphors, m.p. 169-70°.

Experimental

General Method of Preparation.—The solution of the free base (1 mol. proportion) in glacial acetic acid, is added to a solution of oxymethylene-*d*-camphor (1 mol. proportion) when a precipitate usually separates; if not, it is diluted with water; in case any oil separates, it is left overnight when it usually solidifies. It is then crystallised out of methyl alcohol or any suitable solvent (charcoal).

The *laevo* and *racemic* compounds described in the present paper were prepared in the same way as the corresponding *dextro* isomers and have the same crystalline form and similar solubility.

m-Acetylaminoanilinomethylene-*d*-camphor, m.p. 211-13°, shining white needles. [Found: C, 73.03; H, 7.94; $C_{19}H_{24}N_2O_2$ requires C, 73.07; H, 7.69; and N, 8.97 per cent.]. It is very soluble in pyridine, ethyl alcohol and methyl alcohol; less so in chloroform and acetone; sparingly soluble in benzene. The *l*-form, m.p. 211-13°. [Found: N, 9.09.] The *dl*-form, m.p. 216-18°. [Found: N, 9.00.]

Acetylaminoanilinomethylenecamphors (*m* and *p*) were hydrolysed by refluxing with 10–12 per cent. alcoholic potassium hydroxide solution, on the water-bath for three hours:—

m-Aminoanilinomethylene-*d*-camphor, yellowish brown crystalline powder (crystallises when left in vacuum for a week), m.p. 64–65°. [Found: C, 75.36; H, 8.36; and N, 10.66. $C_{17}H_{22}N_2O$ requires C, 75.54; H, 8.15; and N, 10.37 per cent.]. It is freely soluble in the ordinary organic media. The *l*-form, m.p. 64°–65°. [Found: N, 10.47.] The *dl*-form, m.p. 64°–65°. [Found: N, 10.50.]

p-Aminoanilinomethylene-*d*-camphor, yellow needles, m.p. 163–164°. [Found: N, 10.45. $C_{17}H_{22}N_2O$ requires N, 10.37 per cent.] It is freely soluble in the ordinary organic solvents. The *l*-form, m.p. 163–64°. [Found: N, 10.46.] The *dl*-form, m.p. 163–64°. [Found: N, 10.54.]

p-Phenylenebisaminomethylenecamphor (~~*meso*~~ or internally compensated) was prepared by condensing *p*-amino-anilinomethylene-*l*-camphor (m.p. 163–64°) with oxymethylene-*d*-camphor in the usual way and was crystallised out of a mixture of chloroform and absolute alcohol as light yellow needles, melting at 269–70°. [Found: N, 6.67; $C_{28}H_{36}N_2O_2$ requires N, 6.48 per cent.]. It is somewhat soluble in chloroform and pyridine; sparingly soluble in other ordinary solvents. On polarimetric examination the solution of the substance in pyridine was found to be inactive.

Anilinomethylene-*d*-camphor-4-imino-*d*-camphor was prepared by condensing *p*-aminoanilinomethylene-*d*-camphor (m.p. 163–64°) with *d*-camphorquinone on the water-bath in presence of fused sodium sulphate, and obtained as brown amorphous powder from methyl alcohol, melting at 269–70°. [Found N, 6.88; $C_{27}H_{34}N_2O_2$ requires N, 6.70 per cent.]. It is sparingly soluble in the ordinary organic solvents except pyridine.

p-Dimethylaminoanilinomethylene-*d*-camphor, shining yellow fine long needles, m.p. 169–70°. [Found: C, 76.38; H, 8.92 and N, 9.60. $C_{19}H_{26}N_2O$ requires C, 76.51; H, 8.73 and N, 9.40 per cent.] It is freely soluble in the ordinary organic solvents. The *l*-form, m.p. 169–70°. [Found: N, 9.49.] The *dl*-form, m.p. 169–70°. [Found: N, 9.46.]

The rotatory power determinations were made in a 2-*dcm.* jacketed tube at 35°. The value of λ_0 , calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm.

Summary

Aminoanilinomethylenecamphors (*m* and *p*) have been prepared by hydrolysing the condensation products of amino-acetanilides (*m* and *p*) with oxymethylenecamphors (*d*, *l*, *dl*). *p*-Aminodimethylaniline has also been condensed with oxymethylenecamphors. The rotatory power of these compounds is, without exception, found to obey the simple dispersion law of

$$\text{Drude, } [\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}.$$

In the investigations of the effect of constitution on the rotatory power, much difficulty is often met with if we confine the comparison to a single wave-length. For compounds which exhibit simple dispersion, we may overcome this difficulty by comparing the values of their 'absolute specific rotation' which are numerically equal to *k*'s of the Drude equation, when $\lambda = \sqrt{\lambda_0^2 + 1}$ (always in the infra-red region): λ_0 s being the absorption bands of the compounds.

From such a study we notice that the *polar* effect of a substituent group is traceable in the optical activity of these compounds. The substituent influence of the different groups in the order of their decreasing rotatory power is represented by $\text{NH}_2 > \text{N}(\text{CH}_3)_2 > \text{H} > \text{CH}_3 > \text{Cl} > \text{Br} > \text{I}$, which agrees well, subject to minor variations, with the polar series as well as with the sequence of the dissociation constants of the substituted anilines, with which oxymethylenecamphor is condensed.

The effects of *solvents* and *position isomerism* on optical activity are also discussed.

A grateful acknowledgement is made to the Government of Bihar in the Ministry of Education for the grant of a Research Scholarship to one of us (B. B.), which enabled him to take part in this investigation.

TABLE I
m-Acetylaminoanilinomethylenecamphors

Solvent:	Ethyl alcohol	Methyl alcohol	Acetone	Chloroform	Pyridine
Concentration g/100 c.c.	$\frac{d}{l}$ 0.4076 0.4020	0.4000 0.4052	0.4044 0.4000	0.4052 0.4020	0.4000 0.4060
Calculated $\frac{[\alpha]}{\lambda_0}$	$\pm \frac{66.65}{\lambda^2 - 0.1189}$ 0.3448	$\pm \frac{69.10}{\lambda^2 - 0.1189}$ 0.3448	$\pm \frac{63.81}{\lambda^2 - 0.1195}$ 0.3457	$\pm \frac{58.32}{\lambda^2 - 0.1313}$ 0.3623	$\pm \frac{62.81}{\lambda^2 - 0.1202}$ 0.3467
Line	Obs. [α]	Obs. [α]	Obs. [α]	Obs. [α]	Obs. [α]
	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>
Cd ₅₀₈₆	+477.3° -476.3°	+493.8° -494.8°	+458.8° -457.5°	+455.3° -456.5°	+453.8° -453.2°
Ag ₅₂₀₉	438.0 437.8	455.0 453.0	420.4 420.0	417.1 416.6	415.0 416.3
Hg ₅₄₆₁	371.7 370.8	385.0 385.0	357.4 357.5	350.3 349.5	353.8 352.2
Hg ₅₇₈₀	309.2 309.7	321.3 322.0	296.8 296.3	287.5 287.3	293.8 294.4
Na ₅₈₉₃	292.0 291.1	301.3 302.6	279.5 280.0	269.0 270.0	275.6 277.1
Li ₆₁₀₄	262.5 262.5	272.5 272.6	252.3 252.5	241.8 241.3	248.8 248.8
Cd ₆₄₃₈	225.7 225.2	233.8 234.5	216.5 216.3	206.1 206.5	213.8 213.1
Li ₆₇₀₈	201.2 201.5	208.8 208.6	192.9 192.5	182.6 182.8	190.0 190.9
	No mutarota- tion	No mutarota- tion	No mutarota- tion	Solution turned yellow, and showed muta- rotation	No mutarota- tion

TABLE II
m-Aminoanilinomethylenecamphors

Solvent:	Acetone	Methyl alcohol	Benzene	Pyridine	Chloroform
Concentration g/100 c.c.	$\frac{d}{l}$ 0.4040 0.4000	0.4012 0.4052	0.4008 0.4060	0.4056 0.4000	0.4044 0.4000
Calculated $\frac{[\alpha]}{\lambda_0}$	$\pm \frac{73.30}{\lambda^2 - 0.1183}$ 0.3439	$\pm \frac{75.32}{\lambda^2 - 0.1260}$ 0.3550	$\pm \frac{60.16}{\lambda^2 - 0.1263}$ 0.3554	$\pm \frac{73.55}{\lambda^2 - 0.1173}$ 0.3425	$\pm \frac{68.45}{\lambda^2 - 0.1244}$ 0.3527
Line	Obs. [α]	Obs. [α]	Obs. [α]	Obs. [α]	Obs. [α]
	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>
Cd ₅₀₈₆	+522.3° -522.5°	+567.1° -566.5°	+455.3° -454.4°	+509.5° -510.0°
Ag ₅₂₀₉	479.1 478.8	519.7 518.3	415.3 415.0	466.2 466.3
Hg ₅₄₆₁	407.2 407.5	437.4 438.0	349.3 349.8	+406.8° -407.5°	393.1 392.5
Hg ₅₇₈₀	339.2 338.8	361.4 361.6	289.4 289.5	339.0 338.8	326.4 326.3
Na ₅₈₉₃	320.5 320.0	340.3 340.6	271.9 272.2	319.3 320.0	307.8 307.5
Li ₆₁₀₄	288.4 288.8	305.3 306.0	244.5 243.9	288.5 287.5	274.6 276.3
Cd ₆₄₃₈	246.3 247.5	260.4 260.4	208.3 208.2	246.6 247.5	236.2 235.0
Li ₆₇₀₈	221.5 221.3	233.0 233.2	185.9 186.0	221.9 221.3	210.3 210.0
	No mutarota- tion	No mutarota- tion	No mutarota- tion	The solution changed to scarlet red, but exhibited no mutarotation.	No mutarota- tion

TABLE III

p-Acetylaminoanilinomethylenecamphors

Solvent:	Methyl alcohol	Pyridine	Ethyl alcohol	Acetone	Chloroform
Concentration g/100 c.c.	$\frac{d}{l}$ 0.4012 0.4048	0.4016 0.4060	0.4032 0.4000	0.4020 0.4076	0.4040 0.4068
Calculated $\frac{[\alpha]}{\lambda^2}$	$\pm \frac{66.60}{\lambda^2 - 0.1351}$ 0.3676	$\pm \frac{62.97}{\lambda^2 - 0.1339}$ 0.3759	$\pm \frac{67.83}{\lambda^2 - 0.1283}$ 0.3582	$\pm \frac{67.27}{\lambda^2 - 0.1255}$ 0.3543	
Line	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$	Obs. $[\alpha]$
	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i> <i>l</i>	<i>d</i>
Cd ₅₀₈₆	+538.5° -539.7°	+504.2° -503.8°	+518.9° -521.2°	+505.0° -506.3°
Ag ₅₂₀₉	489.9 489.1	458.2 459.4	475.0 473.8	461.5 461.3	
Hg ₅₄₆₁	408.8 407.6	384.7 383.0	400.6 400.0	389.9 388.9	+377.5° -377.5°
Hg ₅₇₈₀	334.7 334.8	313.8 315.3	328.7 328.8	321.7 322.7	308.2 307.2
Na ₅₈₉₃	314.0 313.7	295.0 294.3	310.0 310.0	303.2 303.0	The solution
Li ₆₁₀₄	280.4 281.6	264.0 263.6	276.6 277.5	272.3 271.2	exhibited rapid
Cd ₆₄₃₈	238.0 238.4	224.1 225.4	236.9 237.5	232.6 233.1	mutarotation;
Li ₆₇₉₃	211.9 211.2	199.2 199.6	210.9 210.0	207.9 207.2	the initial
	No mutarota- tion	No mutarota- tion, but solu- tion turned scarlet red on keeping	No mutarota- tion	No mutarota- tion	values, [α] Hg ₅₄₆₁ = 377.5° and [α] Hg ₅₇₈₁ = 308.2° chang- ing to 352.7° and 289.6° re- spectively in course of two hours. Hence readings with other lines we not taken

TABLE IV
p-Dimethylaminoanilinomethylenecamphors

Solvent:	Ethyl alcohol		Acetone		Pyridine	
Concentration $\frac{d}{l}$ g/100 c.c.	0.3992 0.4036		0.4048 0.4012		0.4060 0.4000	
Calculated $\frac{[\alpha]}{\lambda^2}$	$\pm \frac{71.60}{\lambda^2 - 0.1414}$ 0.3760		$\pm \frac{71.45}{\lambda^2 - 0.1395}$ 0.3735			
Line	Obs. $[\alpha]$		Obs. $[\alpha]$		Obs. $[\alpha]$	
	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>
Cd ₅₀₈₆	+610.0°	-611.0°				
Hg ₅₄₆₁	455.9	456.0	+450.9°	-449.9°	+420.1°	-418.8°
Hg ₅₇₈₀	370.8	371.8	366.9	367.6	337.5	336.3
Na ₅₈₉₃	348.2	347.0	343.4	344.0	For 0.40 per cent. chloroform solution, [α] Hg ₅₄₆₁ = +420°. As the solutions in pyridine and chloroform turned scarlet red im- mediately, the readings were taken with much diffi- culty. The change in benzene is so rapid that readings could not be taken.	
Li ₆₁₀₄	309.4	309.8	306.3	305.5		
Cd ₆₄₃₈	263.0	261.5				
Li ₆₇₀₃	231.7	232.9	231.0	230.6		
	No mutarotation		The solution turned deep red on keeping, hence Cd and Ag lines could not be read.			

TABLE V
p-Aminoanilinomethylenecamphors

Solvent :	Concen- tion g/100 c.c.	<i>d</i> or <i>l</i>	[α] Hg ₅₄₆₁	[α] Hg ₅₇₈₀	Remarks
Methyl alcohol ..	0.4012	<i>d</i>	+484.8°	+397.6°	The solutions of the substances in these solvents turned deep red immediately, or after some time. Hence rotatory dispersion could not be studied for more than two lines. In pyridine the change was so rapid, that no readings could be taken.
" ..	0.4040	<i>l</i>	-483.9	-397.1	
Ethyl alcohol ..	0.4020	<i>d</i>	+475.1	+385.7	
" ..	0.4064	<i>l</i>	-475.0	-385.1	
Acetone ..	0.4028	<i>d</i>	+461.8	+378.6	
" ..	0.4007	<i>l</i>	-462.5	-378.8	
Chloroform ..	0.4000	<i>d</i>	+428.8	+353.8	
" ..	0.4056	<i>l</i>	-427.8	-352.7	

TABLE VI

Anilinomethylene-d-camphor-4-imino-d-camphor

Solvent :	Concentration g/100 c.c.	$[\alpha]_{D_{5780}}$	
Pyridine ..	0.0972	+627.3°	Stronger solutions could not be read, and readings with other lines could not be taken as the solution turned deep red at once. The readings in other solvents could not be taken on account of its sparing solubility in them.

REFERENCES

1. B. K. Singh and collaborators .. *J. Ind. Chem. Soc.*, 1931, 8, 345; 1940, 17, 1; *Proc. Ind. Acad. Sci. (A)*, 1937, 6, 340; 1939, 10, 359.
2. Betti .. *Gazz. Chem. Ital.*, 1923, 53, 424; Rule and collaborators, *Journ. Chem. Soc.*, 1924, 1122; 1925, 2188; 1926, 553, 2116; 1927, 54; 1928, 184.
Singh and Bhadhuri .. *Proc. Ind. Acad. Sci. (A)*, 1937, 6, 340; 1939, 10, 359.
3. Perkin .. *Journ. Chem. Soc.*, 1896, 69, 1236.
4. Singh and Bhadhuri .. *J. Ind. Chem. Soc.*, 1930, 7, 774; 1931, 8, 348.
5. ————— .. *Ibid.*, 1930, 7, 550; 1931, 8, 96, 625.
6. ————— .. *Ibid.*, 1932, 9, 109.