

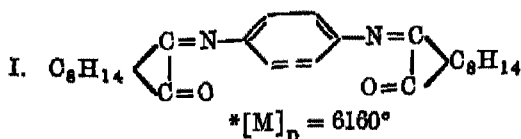
**Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part IX. (a) The Rotatory Dispersion of the Stereoisomeric Oxymethylenecamphors, *p*-Phenylenebisaminomethylenecamphors, and 1:4-Naphthylenebisaminomethylenecamphors. (b) The Structure of Oxymethylenecamphor and the Kinetics of its Mutarotation.**

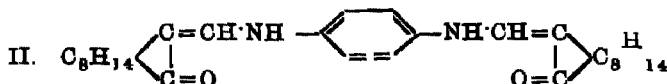
BY BAWA KARTAR SINGH AND BHUTNATH BHADURI.

In the present communication we give an account of our experiments on the optical rotatory dispersion of oxymethylenecamphors and their condensation products with aromatic diamines.

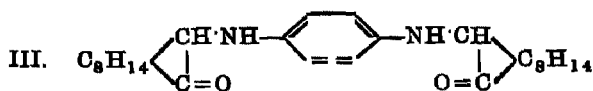
Claisen and his co-workers (*Annalen*, 1894, 281, 331), who discovered *d*-oxymethylenecamphor, also found that this substance undergoes condensation with primary and secondary amines (*loc. cit.*, p. 357). Several of these condensation products were prepared by one of us in 1919 at Lahore, but this work was partly deferred as our studies on the effect of conjugation and position isomerism in the case of derivatives of iminocamphor and bisiminocamphor and their reduction products had not sufficiently advanced. It is now possible to study the effect of conjugation on rotatory power in another way, by comparing the two series of compounds. As in Part VIII, our studies have also been extended to the *l*- and *dl*-isomerides with the object of verifying the assumption of the physical identity of enantiomers.

*The Effect of Unsaturated Conjugation on Rotatory Power.*—On comparing the structural formulae and rotatory power in chloroform of the corresponding derivatives of bisiminocamphor, bisaminomethylenecamphor and bisaminocamphor, striking results emerge:

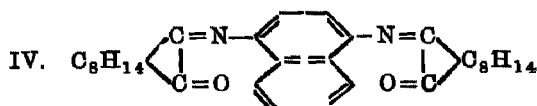




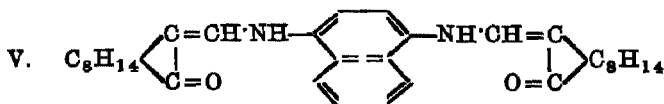
$$[M]_D = 2321^\circ$$



$$* [M]_D = 469^\circ$$



$$*[M]_D = 8145^\circ$$



$$[M]_D = 2746^\circ$$

It is thus 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 (I→III), depression in the 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 (I→II; IV→V).

*The Influence of the Chemical Constitution of the Compound and the Nature of Solvent on the Character of Rotatory Dispersion.*—The simple dispersion formula of Drude,  $[\alpha] = k/(\lambda^2 - \lambda_0^2)$  is valid for a large number of secondary alcohols (Lowry and Dickson, *J. Chem. Soc.*, 1913, 103, 1067) and for nicotine (Lowry and Singh, *Compt. rend.*, 1925, 181, 909; Lowry and Lloyd, *J. Chem. Soc.*, 1929, p. 1772) containing only one asymmetric carbon atom. It is also valid up to the extreme limits of our present experimental methods for the methylcyclohexylideneacetic acid of Pope, Perkin and Wallach (Richards and Lowry, *J. Chem. Soc.*, 1925, 127, 238)

\* These values are taken from Part VIII of this series.

which contains no asymmetric carbon atom. These and other instances show that the simple dispersion formula can be applied to compounds of varied structure. An opportunity is now provided of testing the validity of this simple formula in the case of optically active oxymethylenecamphors and their condensation products with aromatic amino-compounds, in which the elements of simplicity in the molecular structure are absent. These compounds contain two or more asymmetric carbon atoms (*cf.* formulae II and IV) as components of a complex ring system. The striking results of this further test form the subject of the present communication, in which it is shown that in every case the dispersion data can be expressed by a simple equation of the type first put forward by Drude. The remarkable effects which are produced by plotting  $1/[\alpha]$  against  $\lambda^2$  are seen in the very exact straight lines of Figures 1 to 3. A more exact test of the dispersion formula is given by numerical calculation. The tables of rotatory dispersion (VI to XVII) show that the specific rotations, observed and calculated, of oxymethylenecamphor (*d*- and *l*-), *p*-phenylenebisaminomethylenecamphor (*d*- and *l*-), and 1:4-naphthylenebisaminomethylenecamphor (*d*- and *l*-) in different solvents, lie well within the range of possible experimental error. It may be mentioned that oxymethylene-*d*-camphor was first examined in 10 per cent. benzene solution at 20° by Rupe (*Annalen*, 1915, 409, 327) for 4 wave-lengths from a continuous spectrum ( $\lambda=6563, 5898, 5468, \text{ and } 4861$ ). But he failed to discover any simple linear relation between rotatory power and wave-length. Lowry (*J. Chem. Soc.*, 1919, 115, 800) first showed that Rupe's results can be expressed as  $[\alpha] = \frac{22.843}{\lambda^2 - 0.0874}$ . This formula agrees with that obtained by us for the equilibrium value after 48 hours (Table VIII), namely,  $[\alpha] = \frac{22.78}{\lambda^2 - 0.0872}$ . The slight differences in the two formulae are due to the different concentrations and temperatures in the two cases. Our observations are made with 12 wave-lengths from a discontinuous spectrum and over a wider range ( $\lambda=6708 \text{ to } 4358$ ) in 4 solvents. We have also extended our observations to the *l*-enantiomer. In alcohol and benzene, the mutarotation of oxymethylenecamphor was slow, and the dispersion formulae of the freshly prepared solution as well as that in which equilibrium had been attained are given (Tables VI, VII, and VIII). In chloroform and pyridine solutions, the mutarotation could not be

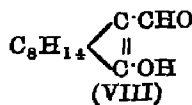
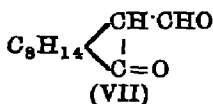
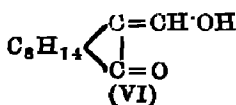
followed owing to its rapidity (Tables IX and X) being almost instantaneous in pyridine, which being basic, acted as a catalyst.

The value of  $\lambda_0$ , the wave-length of the hypothetical absorption band, usually in the ultra-violet region of the spectrum, varies in the initially prepared solution of oxymethylenecamphor and one that has attained equilibrium. In alcohol solution, the value of  $\lambda_0$  decreases from 2975 to 2788 A.U. on keeping, whereas in benzene solution it increases from 2691 to 2987 A.U. (Tables VI, VII, VIII). This increase and decrease in the wave-length of the ultra-violet absorption band in benzene and alcohol respectively may be correlated with the corresponding increase and decrease in the enol-content of the tautomeric mixture of oxymethylenecamphor in the same two solvents (see Tables IV and V).

*p*-Phenylenebisaminomethylenecamphor does not show any mutarotation but 1:4-naphthylenebisaminomethylenecamphor shows slight in chloroform but not in other solvents (Tables XI to XVII).

It may be observed that the rational way of determining the effect of constitution on rotatory power in organic compounds is to study the rotatory dispersion and not to be content with making observations for one wave-length only. To take only two instances from the present data: the specific rotatory power of *p*-phenylenebisaminomethylenecamphor in chloroform solution is lower than that for 1:4-naphthylenebisaminomethylenecamphor for Hg<sub>5461</sub> line but it becomes almost identical for Li<sub>6708</sub> (Tables XI and XIII). On the other hand, this value is almost identical in pyridine for the two compounds for Hg<sub>5461</sub> and it is higher for *p*-phenylenebisaminomethylenecamphor for Li<sub>6104</sub> (Tables XII and XVI). These observations serve to show the inadequacy of deducing the effect of constitution on rotatory power from observations confined to a single wave-length. It is thus clear that only the rotatory dispersion of a compound can give a true picture of the effect of constitution on its rotatory power.

*The Structure of Oxymethylenecamphor and the Kinetics of the Chemical Change Involved in its Mutarotation.*—Claisen (*loc. cit.*) suggested the following structural formulae for oxymethylenecamphor.



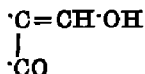
Brühl (*Z. physikal. Chem.*, 1900, **34**, 1), from refractometric determinations, and Federlin (*Annalen*, 1907, **358**, 251), from colorimetric data decided in favour of the structure (VI). Pope and Read (*J. Chem. Soc.*, 1909, **95**, 175) explained the mutarotation of oxymethylenecamphor by assuming that it is a mixture of the two isodynamic forms (VI and VIII). They arrived at this conclusion from the experimental results of Brühl and Federlin. This view of Pope and Read seems to be disproved by the measurements of the percentage of keto- and enol-quantities in oxymethylenecamphor by Meyer's method (*Annalen*, 1911, **380**, 212; *Ber.*, 1911, **44**, 2718; 1912, **45**, 2843). In a freshly prepared benzene solution of oxymethylenecamphor, the percentage of enol at 35° is 32; it increases to 81 in five to six hours (Table IV). This shows that there is a considerable amount of the keto-form in a freshly prepared solution. This result is in agreement with the observations of previous workers who found benzene to be an enolising and alcohol to be a ketonising solvent (Wislicenus, *Ber.*, 1899, **32**, 2837; Brühl, *Ber.*, 1899, **32**, 2826; Meyer, *loc. cit.*; *Ber.*, 1910, **43**, 3044). The value of the velocity constant of mutarotation of oxymethylenecamphor in benzene is nearly identical with that obtained from the progressive determinations of the relative amounts of the enol- and keto-modifications present in the tautomeric mixture by Meyer's method referred to above (Tables I and IV). The close agreement in the value of the velocity constant obtained by these two independent methods conclusively shows that the chemical change involved in the mutarotation of oxymethylenecamphor is of the keto-enol type, and may be represented by the schemes VII→VI or VII→VIII, or by both these changes taking place simultaneously. It is thus clear that the keto-form (VII) is one of the constituents of the tautomeric mixture. The above-mentioned changes are of the monomolecular type, as has been found by experiment. The prototropic changes involved in the mutarotation process are reversible in character. It may therefore be assumed that in benzene solution of oxymethylenecamphor, equilibrium exists between all the three forms. The temperature-coefficient of the velocity constant of mutarotation of oxymethylenecamphor in benzene ( $K_{45^\circ}/K_{35^\circ}$ ) is approximately 29.3 (Table III), being nearly ten times as large as that for an ordinary chemical reaction. It thus appears that the keto-modification of oxymethylenecamphor is very unstable in benzene solution.

The value of the velocity constant of mutarotation of oxymethylene-*l*-camphor for Hg<sub>green</sub> and Hg<sub>yellow</sub> lines is identical (Table II).

The percentage of enol-modification of oxymethylenecamphor in alcohol at 35° was found to be 95.5 in a freshly prepared solution, which falls to 88 in four hours and then remains constant (Table V). Sen and Mondal (*J. Indian Chem. Soc.*, 1928, 5, 609) working at lower temperature (27°) found the enol-percentage in a freshly prepared alcoholic solution of oxymethylenecamphor to be over 98 which decreased to 81 on the fourth day. It thus appears that a freshly prepared alcoholic solution of the substance consists of 100 per cent. enol, specially at a lower temperature. The mutarotation of the substance in alcohol may be represented by one of the following schemes:—VI→VII; VIII→VII; VI→VII→VIII (or *vice versa*).

It has not been possible to calculate the velocity constant of the mutarotation of oxymethylenecamphor in alcohol owing to the very slight decrease in the angle of rotation in the course of 28 hours (see Table VB).

The substance has a definite melting point and crystalline form. It may therefore be assumed that it is homogeneous in the solid state and may be represented by one of the two enolic constitutions (VI or VIII), and in all probability it is constituted as (VI), on account of its acidic character. This structure of oxymethylenecamphor resembles that of formic acid:\*



Oxymethylene compounds.



Formic acid.

Since formic acid is much stronger than any other aliphatic acids it may be concluded that the keto-enol form (VI), would be more acidic than the alternative aldo-enol form, (VIII).

*The Physical Identity of Enantiomers.*—The fact that the rotatory dispersion of the *d*- and *l*-isomerides can be expressed by the same equation is a strong proof of the identity of enantiomers, so

\* For the above-mentioned analogy of formic acid to oxymethylene compounds, we are indebted to Dr. J. C. Bardhan (*private communication*).

far as the magnitude of rotatory power is concerned. The differences in the observed values of rotation for the *d*- and *l*-isomerides are well within experimental error (Tables VI, VII; XI to XVII). The velocity constant of mutarotation of the *d*- and *l*-oxymethylenecamphor in benzene is practically identical (Tables I and II). This shows that the identity of enantiomers with respect to their physical properties (such as rotatory power) extends also to the rate of chemical change involved in the mutarotation of the enantiomers.

The racemic forms of *p*-phenylenebisaminomethylenecamphor and 1:4-naphthylenebisaminomethylenecamphor melt at higher temperature than their optically active isomerides. It follows therefore that the racemic forms are true *dl*-compounds, at least in the solid state.

We wish to reserve the further study of the condensation products of oxymethylenecamphors with amines with the object of elucidating (a) the effect of unsaturated conjugation and position isomerism on optical rotatory power, (b) the character of rotatory dispersion and (c) the extent of the physical identity of enantiomers. The results of this work will be given in subsequent communications.

#### EXPERIMENTAL.

##### *Oxymethylenecamphor* (*d*-, *l*-, *dl*-).

The *d*-isomer was prepared by the method of Bishop, Claisen, and Sinclair (*Annalen*, 1894, 281, 331).

The *l*-isomer was prepared from *l*-camphor in the same way and exhibited properties corresponding with those of its *d*-isomeride. This substance has also been prepared by the same method by Pope and Read (*J. Chem. Soc.*, 1913, 103, 444), who do not give any analytical data. (Found: C, 73.13; H, 8.99.  $C_{11}H_{16}O_2$  requires C, 73.34; H, 8.89 per cent.).

"*Externally compensated oxymethylenecamphor*" was prepared from *dl*-camphor in the same way as its optically active isomerides and has the same crystalline form and similar solubility but melts at 77°-78°. (Found: C, 73.14; H, 8.97.  $C_{11}H_{16}O_2$  requires C, 73.34; H, 8.89 per cent.).

Pope and Read (*loc. cit.*) also prepared this substance by mixing equal weights of the two components (*d*- and *l*-) and found its melting point 80°-81°. We have also prepared it in the same way but find its melting point, 78-79°.

*The Velocity of Mutarotation of Oxymethyleneoamphor (d. and l.) and the Order of the Reaction.*—The velocity constant was determined in benzene at 35° and the reaction was found to be monomolecular; the results obtained are recorded below:

TABLE I.

*Oxymethylene-d-camphor.*

Solvent=benzene; temp. = 35°; length of tube = 2 dcm.

The value of  $K$ , the velocity constant, is calculated from the monomolecular formula,  $K = \frac{2.303}{t_y - t_x} \log \frac{[\alpha]_x - [\alpha]_\infty}{[\alpha]_y - [\alpha]_\infty}$ , the time being expressed in seconds.

1st Sample.	Concentration : g/100 c.c.	Time (minutes).	$[\alpha]_{H_g}$ (gr.)	$K \times 10^4$ .
	1.0008	Initial	Not observed	—
		30	174.9°	—
		63.5	151.4	1.969
		96.5	135.9	1.976
		128	125.9	1.868
		159	119.0	1.938
		∞	103.0	—
2nd Sample		(after 48 hrs.)	Mean	1.944
	0.9975	0	209.0°	—
		31	177.4	1.988
		63.5	154.9	1.919
		99.5	137.3	1.995
		134.5	126.3	1.961
		169.5	120.3	1.945
		218.5	113.8	1.842
		278.5	109.3	1.919
		∞	104.7	—
		(after 48 hrs.)	Mean	1.938

TABLE II.

*Oxymethylene-l-camphor.*

Solvent=benzene ; temp. = 35° ; length of tube = 2 dcm.

	Concentration. g./100 c. c.	Time (minutes).	$[\alpha]$ .	$K \times 10^4$ .
	1.0000	Initial.	Not observed.	—
		25	-183.0°	—
		54	-160.5	1.927
		84.5	-143.5	1.954
		114.5	-132.0	1.911
		142.5	-124.5	1.849
		172.5	-118.5	1.923
		∞	-104.0	—
		(after 48 hrs.)	Mean	1.913

$H_g$  green



TABLE II—Continued.

Concentration :	Time	$[\alpha]$ .	$K \times 10^4$ .
g./100 c. c.	(minutes).		
1.0000	Initial.	Not observed.	
	25	-157.0°	—
	55.5	-137.0	1.988
	84.5	-123.5	1.945
Hg <sub>yellow</sub>	115.5	-113.5	1.904
	150	-108.0	1.868
	182	-101.0	1.919
	$\infty$	-90.0	—
	(after 48 hrs.)		Mean 1.913

Mean value of  $K_{35^\circ}$  (from Tables I and II) =  $1.927 \times 10^{-4}$ .

The velocity constant for the mutarotation in benzene was determined also at  $45^\circ$ . The velocity of the change was so high that the equilibrium was attained within 15 minutes of the preparation of the solution.

TABLE III.

*Oxymethylene-d-camphor.*

Solvent = benzene ; temp. =  $45^\circ$  ; length of tube = 2 dm.

Concentration :	Time	$[\alpha]$ .	$K \times 10^4$ .
g./100 c. c.	(seconds).		
1st Sample, 1.0252	0	127.2°	—
	60	116.5	6.265
	110	110.2	6.265
Hg <sub>green</sub>	200	103.3	5.801
	240	101.4	5.168
	290	99.42	5.504
	$\infty$	93.1	—
2nd Sample, 1.0000	(after 6 hrs.)		Mean 5.798
	( )	137.0°	93.1
	45	128.0	5.665
	85	122.0	5.869
	127	117.0	5.297
	177	112.0	5.787
	233	109.0	5.502
	279	105.5	5.597
Hg <sub>green</sub>	329	103.5	5.367
	395	101.5	5.527
	$\infty$	97.0	—
	(after 6 hrs.)		Mean 5.513

Mean value of  $K_{45^\circ} = 5.655 \times 10^{-3}$  and  $K_{45^\circ} / K_{35^\circ} = 29.3$ .

*Determination of the Relative Amounts of Enol- and Keto-modifications Present in the Tautomeric Mixture of Oxymethylene-d-camphor in Benzene and Alcohol at  $35^\circ$ .*—The experiment was carried out by adding rapidly an alcoholic solution of bromine (the strength

of which was not determined) to the solution of the substance (10 c. c.) cooled to  $-7^{\circ}$ , until the colour was no longer discharged. The excess of bromine was removed by the addition of an alcoholic solution of  $\beta$ -naphthol, excess of potassium iodide was then added, and after warming gently at  $50-55^{\circ}$ , the free iodine was determined by standard thiosulphate solution.

TABLE IV.

*Oxymethylene-d-camphor.*

Solvent=benzene ; sodium thiosulphate=1.015N/10.

The value of  $K$  is calculated from the monomolecular formula given in Table I and substituting  $v$  for  $a$ .

	Concentration : g./100 c. c.	Time (minutes).	Thiosulphate.	Enol.	$K \times 10^4$ .	
1st Sample.	0.9999	0	3.45 c. c.	31.49%	—	
		33	5.30	43.42	2.119	
		68	6.55	59.82	2.065	
		123	7.7	70.34	2.100	
		177	8.25	75.37	2.007	
		$\infty$	8.65	80.63	—	
		(after 6 hrs.)				Mean 2.072
2nd Sample.	0.9975	0	3.55	32.51	—	
		36	5.55	50.83	2.168	
		96	7.40	67.76	2.230	
		156	8.51	74.64	1.985	
		$\infty$	8.90	81.51	—	
		(after 6 hrs.)				Mean 2.123

Mean value of  $K_{25}^{\circ} = 2.10 \times 10^{-4}$ .

TABLE V.

*Oxymethylene-d-camphor.*

Solvent=ethyl alcohol ; sodium thiosulphate=1.015N/10.

A. Concentration :	Time,	Thiosulphate,	Enol.
1.0004 g./100 c. c.	0 min.	10.45 c. c.	95.45%
	88 "	9.85	89.97
	180 "	9.70	87.61
	255 "	9.65	88.14
	24 hrs.	9.65	88.14
	48 "	19.65	88.14

TABLE V—Continued.

Length of the tube.	Concentration : g./100 c. c.	Time.	$\alpha_{D}^{25} / H_R$ (gr.)	$[\alpha]_{D}^{25} / H_R$ (gr.)
2 dcm.	1.0004	0 mins.	4.71°	225.4°
		41 "	4.68	228.0
		124 "	4.65	232.4
		221 "	4.61	230.0
		28 hrs.	4.54	226.4

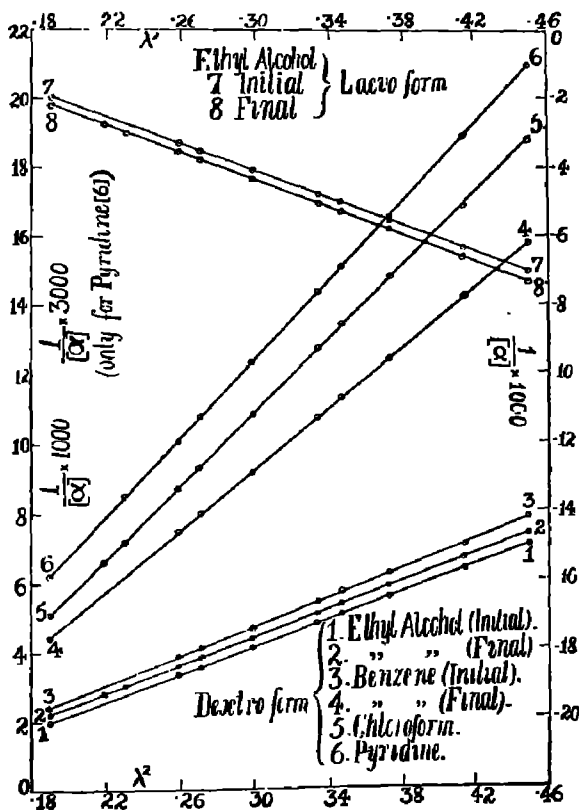


Fig. 1.

Rotatory Dispersion of Ozymethylencamphor (d and l)

*p*-Phenylenebisaminomethylene-*d*-camphor (II).—Oxymethylene-*d*-camphor (0.9 g.) dissolved in alcohol (4–5 c. c.) and *p*-phenylenediamine (0.3 g.) dissolved in 80% acetic acid (4–5 c. c.) were mixed together when a pale yellow precipitate came down immediately. The precipitate was crystallised out of absolute alcohol (after boiling with a little charcoal) as light yellow needles, m. p. 260°–71° (yield, 0.65 g.). It is fairly easily soluble in pyridine; less so in chloroform; difficultly soluble in benzene, acetone; still less soluble in ethyl alcohol and methyl alcohol. (Found: C, 77.77; H, 8.84.  $C_{28}H_{36}O_2N_2$  requires C, 77.78; H, 8.33 per cent.).

The chloroform solution (initially of pale yellow colour) turns to deep scarlet red in 30 minutes.

Rotatory power could be determined in two solvents only, namely, pyridine and chloroform, as it was too insoluble in others to observe the rotation accurately; rotation in pyridine being greater than that in chloroform (Tables XI and XII). *p*-Phenylenebisaminomethylene-*l*-camphor was prepared in the same way as the corresponding *d*-isomer and has the same melting point, solubility, etc.; and also the same rotation within experimental error (Tables XI and XII). (Found: N, 6.65.  $C_{28}H_{36}O_2N_2$  requires N, 6.48 per cent.).

*p*-Phenylenebisaminomethylene-*dl*-camphor was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 278°–75°. (Found: N, 6.65.  $C_{28}H_{36}O_2N_2$  requires N, 6.48 per cent.).

1:4-Naphthylenebisaminomethylene-*d*-camphor (V).—Oxymethylene-*d*-camphor (0.9 g.) dissolved in alcohol (4–5 c. c.) and 1:4-naphthylenediamine hydrochloride dissolved in 80% acetic acid (4–5 c. c.) in presence of a little fused sodium acetate, were mixed together when a yellowish-green precipitate came down at once. The precipitate was crystallised out of absolute alcohol (charcoal) as yellowish-green prisms, m.p. 208°–4°. It is easily soluble in chloroform, pyridine and benzene; less so in acetone; difficultly soluble (in the cold) in ethyl alcohol and methyl alcohol.

The solution of the substance in ordinary organic media is strongly fluorescent (green in the reflected light; yellow in the transmitted light), the fluorescence is however not so marked in ethyl alcohol and methyl alcohol. (Found: N, 6.12.  $C_{32}H_{38}O_2N_2$  requires N, 5.81 per cent.).

The order of rotatory power in different solvents (Tables XIII to XVII) is as chloroform > acetone, ethyl alcohol > pyridine > benzene.

Rotation in methyl alcohol could not be determined as the substance was very difficultly soluble in the solvent at 35°.

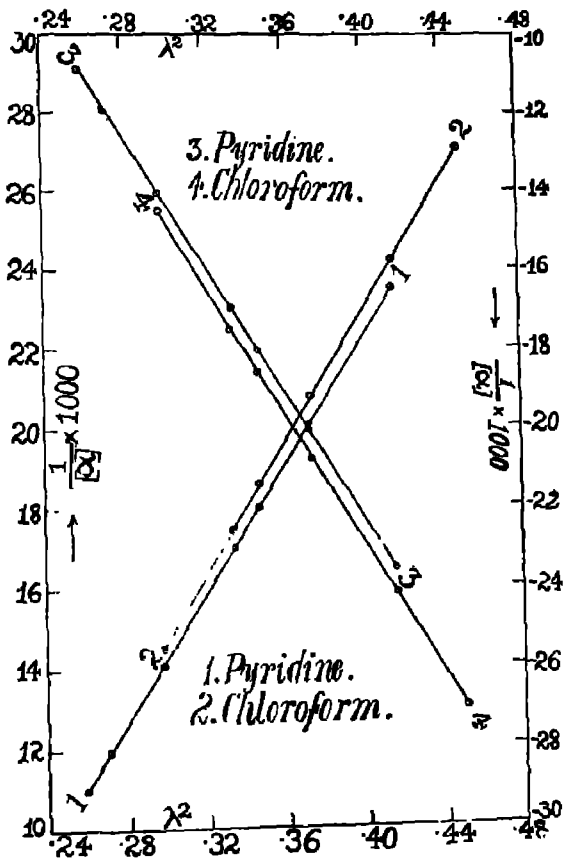


Fig 2.

Rotatory dispersion of *p*-phenylenebisaminomethylene-*d*-camphor.

- d, 1, 2.
- 1, 3, 4.

1 : 4- Naphthylenebisaminomethylene-*l*-cumphor was prepared in the same way as the corresponding *d*-compound and has the same m.p., crystalline form and solubility. (Found: N, 6.05.  $C_{32}H_{36}O_2N_2$ )

requires N, 5.81 per cent). The rotatory power is identical with that of the *d*-isomeride within experimental error (Tables XIII to XVII).

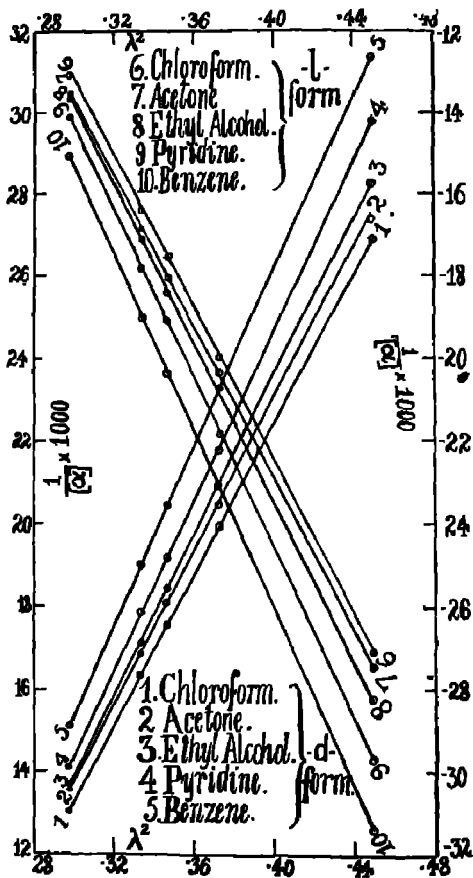


FIG. 8.

Rotatory Dispersion of 1:4-Naphthylensubstituted camphor (*d*- and *l*-).

1.4-Naphthylenebisaminomethylene-dl-camphor was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 220°-222°. (Found N, 6.07. C<sub>32</sub>H<sub>38</sub>N<sub>2</sub>O<sub>2</sub> requires N, 5.81 per cent).

The rotatory power determinations were made in a 2 dcm jacketed tube at 35°. The value of  $\lambda_0$ , calculated from the dispersion formula is given in the tables, and is expressed as  $\mu$ , or 10<sup>-4</sup> cm

TABLE VI.

*Oxymethylenecamphor.*

Solvent = ethyl alcohol (initially).

$$[\alpha] = \pm \frac{51.18}{\lambda^2 - 0.0895}; \quad \lambda_0 = 0.2975.$$

Concn. g / 100 c.c.	<i>Dextro</i>		Line ( $\lambda$ in A.U.).	[ $\alpha$ ]calc = C	<i>Laevo</i>		Concn. g./100 c.c.
	O-C	[ $\alpha$ ]obs. = O.			[ $\alpha$ ]obs = O'	O'-C.	
0.4980	-1.0°	+504.0°	Hg <sub>4368</sub>	±505.0°	-505.8°	+0.3°	0.5008
0.4992	-0.4	300.5	Cd <sub>5086</sub>	300.9	-301.0	+0.1	0.5000
"	+0.4	260.4	Ag <sub>5203</sub>	260.0	-279.0	-1.0	"
0.4980	-1.0	243.1	Hg <sub>5461</sub>	244.1	-243.6	-0.5	0.5008
"	+0.4	208.8	Hg <sub>5760</sub>	208.4	-207.7	-0.7	"
0.5000	+0.8	198.5	Na <sub>5833</sub>	197.7	-198.2	+0.5	0.5020
0.5004	-0.2	179.9	Li <sub>6104</sub>	180.1	-179.4	-0.7	0.4984
0.4992	+0.2	157.2	Cd <sub>6438</sub>	157.0	-157.0	±0	0.5000
0.5004	-0.7	140.9	Li <sub>6708</sub>	141.6	-142.4	+0.8	0.4984

As the substance undergoes mutarotation, a fresh solution was prepared for each wave-length and rotatory power measurements were made within ten minutes of making up the solution

TABLE VII.

*Oxymethylencamphor*

Solvent = ethyl alcohol (after 24 hours)

$$[\alpha] = \pm \frac{50.67}{\lambda^2 - 0.0777}, \quad \lambda_0 = 0.2788$$

Conc g./100 c.c.	<i>Dextro</i>		Line ( $\lambda$ in A U)	[ $\alpha$ ] calc = C	<i>Laevo</i>		Concn g./100 c.c.
	O-C	[ $\alpha$ ] obs -O			[ $\alpha$ ] obs. -O'	O'-O	
0.4980	+1.2°	+452.8°	Hg <sub>4328</sub>	±451.6°	-451.3°	-0.3°	0.4998
0.5004	-1.1	357.8	Cd <sub>4678</sub>	358.9	358.3	-0.6	"
"	-1.1	330.8	Cd <sub>4800</sub>	331.9	332.3	+0.4	"
"	-0.1	279.9	Cd <sub>5028</sub>	280.0	280.2	+0.2	"
"	+1.2	262.9	Ag <sub>5208</sub>	261.7	262.2	+0.5	"
0.4980	+0.1	229.9	Hg <sub>5461</sub>	229.8	229.2	-0.6	"
0.5004	-1.1	227.9	Ag <sub>5458</sub>	229.0	-	-	"
0.4980	+0.6	197.8	Hg <sub>5780</sub>	197.2	197.2	±0	"
0.5000	+0.1	188.0	Na <sub>5893</sub>	187.9	187.2	-0.7	"
0.5004	+0.1	171.9	Li <sub>6104</sub>	171.8	172.1	+0.3	"
"	-0.6	149.9	Cd <sub>6438</sub>	150.5	151.1	+0.6	"
"	+0.8	136.9	Li <sub>6798</sub>	136.1	136.1	±0	"

TABLE VIII

*Oxymethylene d camphor in Benzene**Initially.**After 48 hours.*

$$[\alpha] = \frac{48.39}{\lambda^2 - 0.0724}, \quad \lambda_0 = 0.2691 \quad [\alpha] = \frac{22.78}{\lambda^2 - 0.0892}; \quad \lambda_0 = 0.2987$$

Conc g/100 c.c.	O-C	[ $\alpha$ ] calc. = C	[ $\alpha$ ] obs = O	Line	[ $\alpha$ ] obs = O	[ $\alpha$ ] calc = C'	O-C'	Conc g/100 c.c.
0.4992	+1.0°	+411.8°	+415.7°	Hg <sub>4328</sub>	+227.4°	+225.2°	+1.2°	0.4992
0.4996	-0.5	259.7	259.2	Cd <sub>5028</sub>	134.2	134.4	-0.2	"
"	-0.1	243.3	243.2	Ag <sub>5209</sub>	125.2	125.1	+0.1	"
0.4992	±0	214.3	214.3	Hg <sub>6461</sub>	109.1	109.0	+0.1	"
"	+0.4	184.9	185.3	Hg <sub>6780</sub>	93.1	93.0	+0.09	"
0.5000	±0	176.0	176.0	Na <sub>5893</sub>	88.1	88.2	-0.14	"
0.5004	-1.3	161.2	159.9	Li <sub>6104</sub>	80.1	80.3	-0.24	"
"	+0.4	141.5	141.9	Cd <sub>6438</sub>	70.1	70.0	+0.09	"
"	-0.2	128.1	127.9	Li <sub>6798</sub>	63.1	63.1	-0.02	"



TABLE IX.

*Oxymethylene-d-camphor in Chloroform (after 24 hours).*

$$[\alpha] = \frac{18.80}{\lambda^2 - 0.0947}; \lambda_0 = 0.8078.$$

Concentration. g./100 c.c.	Line.	$[\alpha]$ obs. = O.	$[\alpha]$ calc. = C.	O - C.
0.4980	Hg <sub>4358</sub>	+196.8°	+197.5°	-0.7°
"	Cd <sub>4678</sub>	151.6	151.6	±0
"	Cd <sub>4800</sub>	139.5	139.6	+0.1
"	Cd <sub>5086</sub>	114.5	114.7	-0.2
"	Ag <sub>5209</sub>	107.4	106.4	+1.0
"	Hg <sub>5481</sub>	92.37	92.34	+0.03
"	Hg <sub>5780</sub>	78.30	8.64	-0.34
"	Ni <sub>5893</sub>	74.29	74.49	-0.20
"	Li <sub>6104</sub>	67.36	67.66	-0.40
"	Cd <sub>6438</sub>	59.23	5.79	+0.44
"	Li <sub>6708</sub>	53.21	52.21	+0.80

The mutarotation in chloroform is too rapid to observe readings accurately in the initial stages; so much so that the initial rotation  $[\alpha]_{\text{Hg}(gr)} = 172.7^\circ$  falls to  $108.4^\circ$  in course of 20 minutes, the equilibrium value  $92.37^\circ$  being attained in next half an hour or so.

TABLE X.

*Oxymethylene-d-camphor in Pyridine.*

$$[\alpha] = \frac{52.85}{\lambda^2 - 0.0811}; \lambda_0 = 0.2848.$$

Concentration : g./100 c.c.	Line.	$[\alpha]$ obs. = O.	$[\alpha]$ calc. = C.	O - C.
0.5008	Hg <sub>4358</sub>	+484.2°	+486.2°	-1.0°
"	Cd <sub>4800</sub>	353.4	353.9	-0.5
"	Cd <sub>5086</sub>	297.5	297.8	-0.3
"	Ag <sub>5209</sub>	278.0	277.8	+0.2
"	Hg <sub>5481</sub>	242.6	243.4	-0.8
"	Hg <sub>5780</sub>	208.8	208.8	-0.2
"	Ni <sub>5893</sub>	198.7	198.6	+0.1
"	Li <sub>6104</sub>	181.7	181.3	+0.4
"	Cd <sub>6438</sub>	158.7	158.3	+0.4
"	Li <sub>6708</sub>	142.7	143.3	-0.6

Initial and final readings were the same.

TABLE XI.

*p*-Phenylenebisaminomethylenecamphor in Chloroform.

$$[\alpha] = \pm \frac{11t \cdot 8}{\lambda^2 - 0 \cdot 1254}; \quad \lambda_0 = 0 \cdot 8542.$$

Concn. g./100 o.c.	<i>Dextro</i>		Line.	[ $\alpha$ ] calc. = C.	<i>Laevo</i>		Concn. g./100 o.c.
	O-C.	[ $\alpha$ ] obs. = O.			[ $\alpha$ ] obs. = O'.	O'-C.	
0-0820	-1.5°	+689.2°	Hg <sub>5461</sub>	±690.7°	-690.2°	-0.5°	0-0804
"	+1.4	573.2	Hg <sub>5780</sub>	571.8	572.2	+0.4	"
"	-1.2	586.7	Na <sub>5893</sub>	587.9	587.5	-0.4	0-0800
0-0800	-1.4	481.3	Li <sub>6104</sub>	482.7	480.3	-2.4	0-0812
"	-0.8	412.5	Cd <sub>6438</sub>	412.8	413.5	+0.7	"
"	+1.0	368.7	Li <sub>6703</sub>	367.7	369.5	+1.8	"

The solution initially of pale yellow colour changes to scarlet red with time. Readings were taken with fresh solutions almost with every line.

TABLE XII.

*p*-Phenylenebisaminomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{124 \cdot 8}{\lambda^2 - 0 \cdot 1225}; \quad \lambda_0 = 0 \cdot 8500.$$

Concn. g./100 o.c.	<i>Dextro</i>		Line.	[ $\alpha$ ] calc. = C.	<i>Laevo</i>		Concn. g./100 o.c.
	O-C.	[ $\alpha$ ] obs. = O.			[ $\alpha$ ] obs. = O'.	O'-C.	
0-0800	-3.1°	+912.5°	Cd <sub>6086</sub>	±915.6°	-917.5°	+1.9°	0-0812
"	-0.6	887.5	Ag <sub>5209</sub>	898.1	887.3	-0.8	"
"	+2.6	712.5	Hg <sub>5461</sub>	709.9	710.9	+1.0	0-0816
"	-1.8	587.5	Hg <sub>5780</sub>	589.3	588.8	-1.0	"
"	+1.4	556.8	Na <sub>5893</sub>	554.9	554.2	-0.7	0-0812
"	+1.4	500.0	Li <sub>6104</sub>	498.6	498.7	+0.1	"
"	-1.6	425.0	Cd <sub>6438</sub>	426.8	424.8	-2.0	"

There was no mutarotation or change in colour with lapse of time (compare the same in chloroform).

TABLE XIII.

1:4-Naphthylenebisaminomethylenecamphor in Chloroform.

$$[\alpha] = \pm \frac{109.0}{\lambda^2 - 0.1558}; \quad \lambda_0 = 0.3947.$$

<i>Dextro</i>			Line.	[ $\alpha$ ] calc. = C.	<i>Laevo</i>		
Concn. g./100 c.c.	O-C.	[ $\alpha$ ] obs. = O.			[ $\alpha$ ] obs. = O'.	O'-C.	Concn. g./100 c.c.
0.0808	+2.2°	+767.4°	Hg <sub>5461</sub>	±765.2°	-764.9°	-0.3°	0.0804
"	+1.5	612.6	Hg <sub>5730</sub>	611.1	609.4	-1.7	"
0.0800	-0.8	569.4	Na <sub>5893</sub>	569.7	569.9	+0.2	0.0816
0.0808	-1.2	501.3	Li <sub>6104</sub>	502.5	500.0	-2.5	0.0800
"	+1.0	371.4	Li <sub>6703</sub>	370.4	368.8	-1.6	"

The chloroform solution undergoes slight mutarotation, the initial value [ $\alpha$ ]<sub>Hg(5461)</sub> = 767.4° changing to 780.4° in course of two and a half hours. After 24 hours the colour was too dark to be read.

TABLE XIV.

1:4-Naphthylenebisaminomethylenecamphor in Acetone.

$$[\alpha] = \pm \frac{108.9}{\lambda^2 - 0.1506}; \quad \lambda_0 = 0.3881.$$

<i>Dextro</i>			Line.	[ $\alpha$ ] calc. = C.	<i>Laevo</i>		
Concn. g./100 c.c.	O-C.	[ $\alpha$ ] obs. = O.			[ $\alpha$ ] obs. = O'.	O'-C.	Concn. g./100 c.c.
0.0800	-0.4°	+737.5°	Hg <sub>5461</sub>	±737.9°	-737.5°	-0.4°	0.0800
"	+0.5	593.8	Hg <sub>5730</sub>	593.8	593.8	+0.5	"
0.0804	-0.7	558.5	Na <sub>5893</sub>	554.2	554.2	±0	0.0812
0.0808	-1.6	488.9	Li <sub>6104</sub>	490.5	491.5	+1.0	0.0824
"	+1.7	365.4	Li <sub>6703</sub>	363.7	364.1	+0.4	"

There was no mutarotation observed on keeping the solution for 24 hours, though the solution had acquired red colour.

TABLE XV.

1:4-Naphthylenebisaminomethylenecamphor in Ethyl Alcohol.

$$[\alpha] = \pm \frac{103.5}{\lambda^2 - 0.1571} ; \lambda_0 = 0.8964.$$

Concn. g./100 c.c.	<i>Dextro</i>		Line.	[ $\alpha$ ]calc. =C.	<i>Laevo</i>		Concn. g./100 c.c.
	O-C.	[ $\alpha$ ]obs. =O.			[ $\alpha$ ]obs. =C'.	O'-C.	
0.0804	+0.3*	+733.8*	Hg <sub>5461</sub>	$\pm 733.5^\circ$	-734.4°	+0.9*	0.0800
"	-0.1	584.5	Hg <sub>5720</sub>	584.6	584.4	-0.2	"
0.0800	-0.8	543.8	Na <sub>5833</sub>	544.6	543.8	-0.8	"
0.0804	-1.5	478.8	Li <sub>4104</sub>	480.3	481.6	+1.3	0.0824
"	+1.1	354.5	Li <sub>4708</sub>	359.4	353.7	+0.3	"

There was no change in rotation even after 3 hours.

TABLE XVI.

1:4-Naphthylenebisaminomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{97.40}{\lambda^2 - 0.1606} ; \lambda_0 = 0.4008.$$

Concn. g./100 c.c.	<i>Dextro</i>		Line.	[ $\alpha$ ]calc. =C.	<i>Laevo</i>		Concn. g./100 c.c.
	O-C.	[ $\alpha$ ]obs. =O.			[ $\alpha$ ]obs. =O'.	O'-C.	
0.0804	+1.0*	+708.9*	Hg <sub>5461</sub>	$\pm 707.9^\circ$	-708.1°	+0.2*	0.0812
"	-1.7	559.7	Hg <sub>5720</sub>	561.4	560.2	-1.2	"
"	$\pm 0$	522.4	Na <sub>5833</sub>	522.4	523.4	+1.0	"
"	+0.7	480.2	Li <sub>4104</sub>	459.5	457.4	-2.1	0.0820
"	+0.8	335.8	Li <sub>4708</sub>	336.6	335.5	-1.1	"

The solution did not undergo any mutarotation.

TABLE XVII.

1:4-Naphthylenebisaminomethylencamphor in Benzene.

$$[\alpha] = \pm \frac{92.47}{\lambda^2 - 0.1684} ; \lambda_0 = 0.3980.$$

Concn. g./100 c.c.	<i>Dextro</i>		Line.	[ $\alpha$ ] calc. = C.	<i>Laevo</i>		Concn. g./100 c.c.
	O-C.	[ $\alpha$ ] obs. = O.			[ $\alpha$ ] obs. = O'.	O'-C.	
0.0816	+0.3°	+661.8°	Hg <sub>6441</sub>	+661.5°	-662.5°	+1.0°	0.0800
"	+0.6	527.0	Hg <sub>6760</sub>	526.4	525.0	-1.4	"
"	+0.3	490.3	Na <sub>5893</sub>	490.0	491.2	+1.2	0.0804
"	-1.8	429.9	Li <sub>4114</sub>	431.7	431.3	-0.4	0.0800
"	+1.4	318.6	Li <sub>4703</sub>	317.2	318.8	+1.6	"

There was no change in rotation even after 24 hours.

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