STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXVII. The Rotatory Dispersion of Stereoisomeric 2 : 5-Dichloroanilino-, 3-Nitro-4-chloroanilino-, 2-Nitro *p*-toluidino- and 4-Nitro-*o* toluidino methylenecamphors

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IN continuation of our studies, Part XXIV in this series,[1] we have now investigated the rotatory dispersion of the condensation products of oxymethylenecamphors (*d*, *l*, *dl*) and 2:5-dichloroaniline, 3-nitro-4-chloroaniline, 2-nitro-*p*-toluidine and 4-nitro-*o*-toluidine.

INFLUENCE OF CHEMICAL CONSTITUTION ON ROTATORY DISPERSION

Rotatory dispersions may be classified as "Simple" or "Complex" according as they can, or cannot, be expressed by Drude's one-term equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$. The condensation products of oxymethylenecamphors and aromatic amines, described here, were found to obey the simple dispersion formula exactly. On plotting $\frac{1}{[\alpha]}$ against λ^2, exact straight lines were obtained (Fig. 1).

Out of 430 observations recorded in this paper (Tables III–VI), in as many as 398 cases the difference (*o–c*) between the observed (*o*) and the calculated (*c*) values of specific rotation corresponds to a difference of 0·02° or less in the corresponding angles of rotation. In 22 cases this difference lies between 0·02° and 0·03°, and only in 10 cases, most of which are for Hg_{4358} (Mercury violet)—a difficult line to read—this difference lies between 0·03° and 0·05°. All these differences (*o–c*), not given here for economy of space, are, however, of the nature of casual experimental errors.

PHYSICAL IDENTITY OF ENANTIOMERS

Pasteur's Law of Molecular Dissymmetry, according to which the *d*- and *l*-forms of a substance possess identical physical properties as regards their magnitude has been found to hold good: the values of the rotatory power of the *d*- and *l*-forms of the compounds in different solvents (Tables III–VI) are identical within the limits of experimental error.

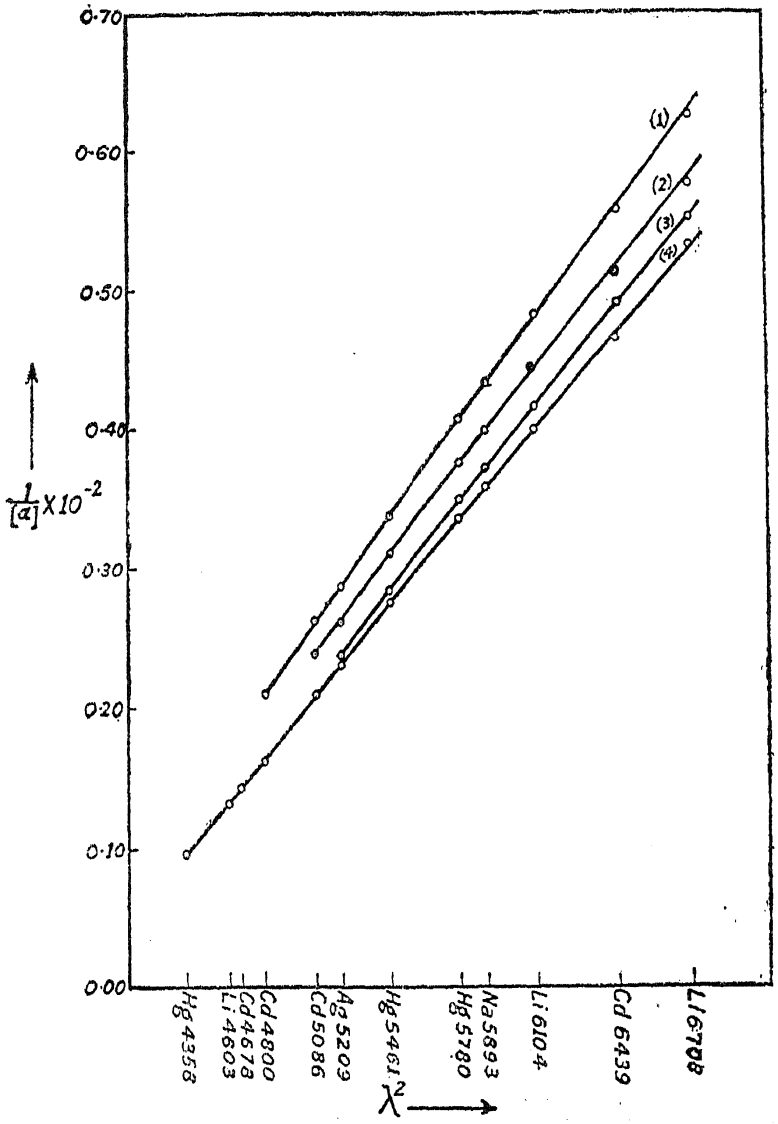


FIG. 1

(1) 2-Nitro-*p*-toluidinomethyl ene-*d*-camphor in benzene.
(2) 3-Nitro-4-chloroanilinomethyl ene-*d*-camphor in chloroform.
(3) 4-Nitro-*o*-toluidinomethyl ene-*d*-camphor in methyl alcohol.
(4) 2 : 5-Dichloroanilinomethyl ene-*d*-camphor in methyl alcohol.

EFFECT OF THE NATURE OF THE SUBSTITUENT GROUP ON THE ROTATORY POWER

The polar effect of substituent group is traceable in optical activity.[1,2]

In the present investigation we have studied the effect on rotation of three substituents, Cl, CH_3 and NO_2 groups, which are assigned polarities in accordance with the following polar series[3] deduced from specific inductive capacities: $\overset{-}{O}H$, Cl, Br, I, C_2H_5, $\overset{-}{C}H_3$, $\overset{+}{H}$, CO_2H, CHO, $COCH_3$, CN, $\overset{+}{N}O_2$. From this study it is found that the effect of substituents on the rotatory power can be generally correlated with their polarities as is evident from the following account:—

(1) Cl, on account of its negative polarity, lowers the rotatory power of the parent compound as supported by the following observations (Table I):

TABLE I

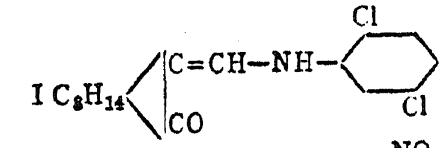
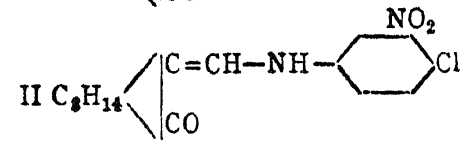
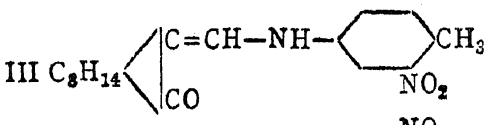
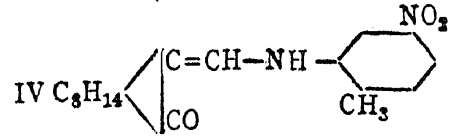
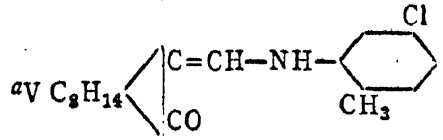
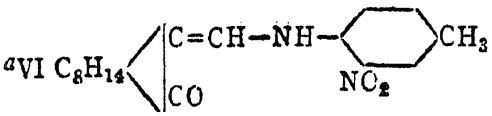
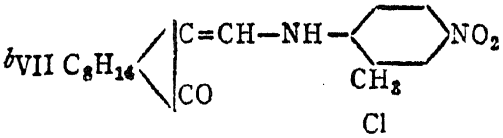
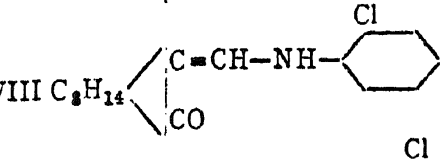
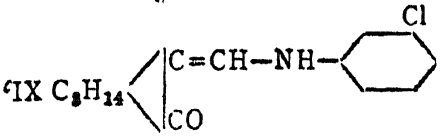
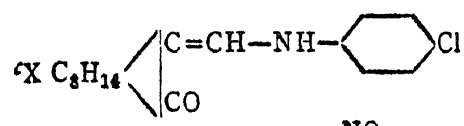
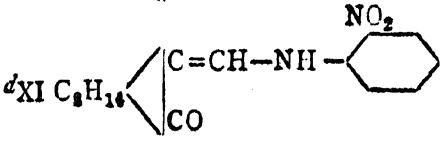
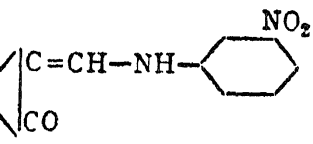
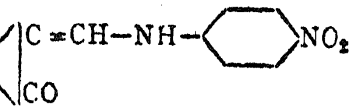
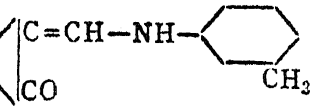
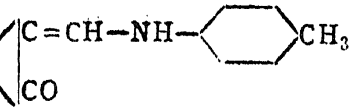
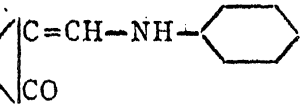
Structural formulæ	$[\alpha]^{35°\,C.}_{Hg_{5461}}$					
	MeOH 31·2*	EtOH 25·8*	Acetone 21·5*	Pyridine 12·4*	Chloroform 5·2*	Benzene 2·28*
 I C_8H_{14}	360·0° (60·17)	351·0° (57·76)	352·0° (58·11)	358·0° (59·45)	356·0° (57·76)	344·0° (56·94)
 II C_8H_{14}	380·0 (65·59)	365·0 (65·32)	360·0 (64·45)	350·0 (61·69)	320·0 (57·11)	290·0 (54·14)
 III C_8H_{14}	388·0 (66·68)	376·0 (66·21)	368·0 (65·54)	362·0 (65·02)	330·0 (61·26)	295·0 (52·39)
 IV C_8H_{14}	350·0 (57·16)	352·0 (57·8)	355·0 (58·58)	370·0 (58·03)	353·0 (56·38)	339·0 (56·24)
 [a]V C_8H_{14}	386·0 (62·6)	378·0 (60·7)	380·0 (62·5)	390·0 (63·6)	373·0 (60·4)	361·0 (58·5)
 [a]VI C_8H_{14}	492·9† (65·46)	459·5† (62·44)	464·1† (60·26)	416·4† (57·32)	458·5† (64·16)	390·0 (59·45)
 [b]VII C_8H_{14}	491·8 (70·4)	500·7 (67·43)	522·1 (70·01)	561·5 (70·2)	523·3 (66·63)	479·4 (66·71)
 [c]VIII C_8H_{14}	400·2 (64·77)	405·8 (72·23)	380·0 (61·42)	391·3 (63·72)	386·0 (61·79)	364·7 (57·76)
 [c]IX C_8H_{14}	388·5 63·14	384·7 (62·47)	388·0 (63·65	374·4 (63·70)	381·4 (61·22)	363·6 60·73)
 [c]X C_8H_{14}	417·7 (75·34)	406·3 (73·20)	401·8 (70·58)	394·4 (68·19)	374·6 (67·56)	359·4 (57·80)
 [d]XI C_8H_{14}	493·1† (57·80)	.. ..	468·1† (59·07)	424·8† (72·06)	484·† (45·54	399·2 (50·26)

TABLE I—(*Contd.*)

Structural formulæ	$[\alpha]^{35°\,C.}_{Hg_{5461}}$					
	MeOH 31·2*	EtOH 25·8*	Acetone 21·5*	Pyridine 12·4*	Chloroform 5·2*	Benzene 2·28*
[d]XII C_8H_{14} 	393·9° (79·36)	.. ..	389·2° (69·47)	367·1° (69·80	350·0° (68·63)	315·6° (57·73)
[d]XIII C_8H_{14} 	510·7 (77·47)	.. ..	519·4 (74·11)	545·0 (79·58)	493·5 (74·49)	437·0 (68·05)
[e]XIV C_8H_{14} 	454·4 (85·21)	439·9° (81·02)	442·3 (82·31)	405·8 (80·48)	384·8 (68·55)	352·6 (71·37)
[e]XV C_8H_{14} 	465·0 (79·56)	440·8 (80·13)	425·8 (78·77)	401·6 (74·15)	401·6 (74·15)	355·4 (66·65)
[e]XVI C_8H_{14} 	480·0 (86·78)	451·3 (81·83)	448·9 (83·08)	433·2 (81·21)	424·6 (78·57)	367·1 (70·71)

* Dielectric constant of the solvent.

† Calculated value from the dispersion formula.

[a] B. K. Singh and R. K. Tewari, *Proc. Indian Acad. Sci.*, 1945, 22 A, 20.

[b] B. K. Singh and A. B. Lal, *Ibid.*, 1940, 12A, 157.

[c] B. K. Singh and B. Bhaduri, *Ibid.*, 1937, 6A, 340.

[d] B. K. Singh and T. P. Barat, *J. Indian Chem. Soc.*, 1940, 17, 1.

[e] B. K. Singh, B. Bhaduri and T. Barat, *Ibid.*, 1931, 8, 345.

the rotatory power of 2:5-dichloroanilinomethylenecamphor (I) is lower than that of *o*- and *m*-chloroanilinomethylenecamphors (VIII, IX); the rotatory power of 3-nitro-4-chloroanilinomethylenecamphor (II) is lower than that of *m*-nitroanilinomethylenecamphor (XII); and the rotatory power of *o*-, *m*-, and *p*-chloroanilinomethylenecamphors (VIII, IX, X) is lower than that of anilinomethylenecamphor (XVI) in all the solvents. (2) CH_3 group also, on account of its negative polarity, has a lowering effect on the rotatory power of the parent compound as is evident from the following observations (Table I): the rotatory power of 2-nitro-*p*-toluidinomethylenecamphor (III) is lower than that of *m*-nitroanilinomethylenecamphor (XII); the rotatory power of 3-nitro-*p*-toluidinomethylenecamphor (VI) is lower than that of *o*-nitroanilinomethylenecamphor (XI); and the rotatory power of *m*-and

p-toluidinomethylenecamphors (XIV, XV) is lower than that of anilinomethylenecamphor (XVI) in all the solvents; the rotatory power of 4-chloro-*o*-toluidinomethylenecamphor (V) is lower than that of *m*-chloroanilinomethylenecamphor (IX) in five solvents but *higher* in pyridine. There are, however, some deviations from the abovementioned generalization: the rotatory power of 4-nitro-*o*-toluidinomethylenecamphor (IV) is lower than that of *m*-nitroanilinomethylenecamphor (XII) in three solvents but *higher* in pyridine, chloroform and benzene; the rotatory power of 5-nitro-*o*-toluidinomethylenecamphor (VII) is lower than that of *p*-nitroanilinomethylenecamphor (XIII) in methyl alcohol but *higher* in acetone, pyridine, chloroform and benzene. (3) On the other hand, the positive-polarity of NO_2 group should raise the rotatory power of the parent compound. This is supported by the following observations (Table I): the rotatory power of 3-nitro-*p*-toluidinomethylenecamphor (VI) is higher than that of *p*-toluidinomethylenecamphor (XV), and the rotatory power of *p*-nitroanilinomethylenecamphor (XIII) is higher than that of anilinomethylenecamphor (XVI) in all the solvents; the rotatory power of *o*-nitroanilinomethylenecamphor (XI) is higher than that of anilinomethylenecamphor (XVI) in all the solvents except pyridine in which it is lower. But in the following three cases the NO_2 group is found to have a lowering effect on the rotatory power: the rotatory power of 3-nitro-4-chloroanilinomethylenecamphor (II) is lower than that of *p*-chloroanilinomethylenecamphor (X); the rotatory power of 2-nitro-*p*-toluidinomethylenecamphor (III) is lower than that of *p*-toluidinomethylenecamphor (XV); and the rotatory power of *m*-nitroanilinomethylenecamphor (XII) is lower than that of anilinomethylenecamphor (XVI) in all the solvents.

The effect of polarity of the substituent group is, with minor deviations, thus traceable in optical activity.

The position of the substituent group has also an effect on the rotatory power and is brought out in the following cases: 3-nitro-*p*-toluidinomethylenecamphor (VI), in which the NO_2 group is in the *o*-position to the substituted amino-group, has a higher rotatory power, whereas 2-nitro-*p*-toluidinomethylenecamphor (III) in which it is in the *m*-position to the substituted amino-group, has a lower rotatory power than that of *p*-toluidinomethylenecamphor (XV). Similarly, the rotatory power of *o*-nitroanilinomethylenecamphor (XI) and *p*-nitroanilinomethylenecamphor (XIII) is higher (except in pyridine in the former case), whereas the rotatory power of *m*-nitroanilinomethylenecamphor (XII) is lower than that of anilinomethylenecamphor (XVI). The NO_2 group raises the rotatory power when it is in

the *o*- or *p*-position to the substituted amino-group, whereas it lowers it when it is in the *m*-position.

EFFECT OF THE NATURE OF THE SOLVENT ON THE ROTATORY POWER

The specific rotatory power of these compounds for Hg_{5461} in six solvents is given in Table I. The sequences of decreasing rotatory power are as follows:—2:5-dichloroanilinomethylenecamphor (I): methyl alcohol > pyridine > chloroform > acetone > ethyl alcohol > benzene; 3-nitro-4-chloroanilinomethylenecamphor (II): methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene; 2-nitro-*p*-toluidinomethylenecamphor (III): methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene; 4-nitro-*o*-toluidinomethylenecamphor (IV): pyridine > acetone > chloroform > ethyl alcohol > methyl alcohol > benzene. The sequence of decreasing (or increasing) rotatory power runs in the cases of 3-nitro-4-chloroanilinomethylenecamphor (II) and 2-nitro-*p*-toluidinomethylenecamphor (III) strictly parallel with that of the dielectric constants of the solvents, namely, methyl alcohol (31·2) > ethyl alcohol (25·8) > acetone (21·5) > pyridine (12·4) > chloroform (5·2) > benzene (2·28). A similar but less marked parallelism can be traced in the case of the other two compounds also, namely, the rotatory power of 2:5-dichloroanilinomethylenecamphor (I) is highest in methyl alcohol, which has the highest dielectric constant, and lowest in benzene, which has the lowest dielectric constant, and the rotatory power of 4-nitro-*o*-toluidinomethylenecamphor (IV) is lowest in benzene.

It would, however, seem more rational to compare the rotatory power of a substance with the dielectric constant of its solution, and not of the solvent in which its rotatory power is determined. We have used the values of the dielectric constants of the solvents as we have not at our disposal the values of the dielectric constants of the solutions.

The abovementioned sequences of rotatory power in the different solvents are derived from the rotatory power measurements for Hg_{5461} (Table I). The choice of this wave-length is purely arbitrary as different sequences are obtained for other wave-lengths. For example, in the case of 4-nitro-*o*-toluidinomethylenecamphor (IV) the sequence for Hg_{5461} is pyridine > acetone > chloroform > ethyl alcohol > methyl alcohol > benzene, whereas that for Na_{5893} is pyridine > ethyl alcohol > acetone > methyl alcohol > chloroform > benzene. These effects of dispersion can, however, be eliminated when compounds are found to obey the simple dispersion equation of Drude, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$. The rotation-constant (K) of this one-term equation can

be used as a measure of the absolute rotatory power of the substance. It refers to a wave-length λ, where $\lambda^2 - \lambda_0^2 = 1$ square micron, and it is not very much greater than 10,000 Å.U. The longest observed wave-length in our measurements is L_{6708}^{i} and an extrapolation from it to about 10,000 Å.U. is easily permissible in view of the linear nature of the dispersion equations obtained from our measurements. We have, therefore, also given in brackets (Table I) the values of K, the rotation-constant, as a measure of the absolute rotatory power of the compounds.

It will be seen that the value of K (Table I) in the different solvents runs parallel with that of the dielectric constant of the solvent in the case of 3-nitro-4-chloroanilinomethylenecamphor (II) and 2-nitro-*p*-toluidinomethylenecamphor (III). In the case of the other two compounds (I, IV) there is less strict parallelism: the value of K for 2:5-dichloroanilinomethylenecamphor (I) is lower in ethyl alcohol and higher in pyridine, and for 4-nitro-*o*-toluidinomethylenecamphor (IV) it is lower in methyl and ethyl acohols than the sequence of the dielectric constants of the solvents warrants it. This further emphasizes that the value of the dielectric constant of the solution rather than that of the solvent should be compared with the absolute rotatory power of the solution.

The compounds listed above in Table II are optically active nitro-dyes. They vary in colour from yellow to orange in the solid state or in alcoholic solution. When their alcoholic solution is made alkaline, the colour deepens in the case of the *ortho*- and *para*-nitro compounds (VI and VII,

EFFECT OF THE POSITION OF THE NITRO-GROUP ON THE COLOUR OF THE DYES

TABLE II

Substances	Colour in the solid state	Colour in ethyl alcohol	Colour in ethyl alcohol in presence of KOH
3-Nitro-*p*-toluidinomethylenecamphor (VI, Table I)	Orange-red	Yellow-orange	Port-wine-red
5-Nitro-*o*-toluidinomethylenecamphor (VII, Table I)	Bright yellow	Yellow	Deep violet
3-Nitro-4-chloroanilinomethylenecamphor (II, Table I)	Bright yellow	Lemon-yellow	Port-wine-red
2-Nitro-*p*-toluidinomethylenecamphor (III, Table I)	Lemon-yellow	Lemon-yellow	Yellow-orange
4-Nitro-*o*-toluidinomethylenecamphor (IV, Table I)	Lemon-yellow	Lemon-yellow	Yellowish-light-brown

TABLE III. 2: 5-*Dichloroanilinomethylenecamphors*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentratration in gm./100 c.c. $\begin{cases} d \\ l \end{cases}$	0·5000 0·5000		0·5000 0·5000		0·5000 0·5000		0·5000 0·5000		0·5000 0·5000		0·5000 0·5000	
Calculated $\begin{cases} [\alpha] \\ \lambda_0 \end{cases}$	$\pm \frac{60\cdot17}{\lambda^2-0\cdot1319}$ 0·3631		$\pm \frac{57\cdot76}{\lambda^2-0\cdot1342}$ 0·3664		$\pm \frac{58\cdot11}{\lambda^2-0\cdot1338}$ 0·3658		$\pm \frac{59\cdot45}{\lambda^2-0\cdot1327}$ 0·3643		$\pm \frac{57\cdot76}{\lambda^2-0\cdot1355}$ 0·3681		$\pm \frac{56\cdot94}{\lambda^2-0\cdot1326}$ 0·3641	
Line λ	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Hg_{4358} ..	+1038·0°	−1032·0°	+1031·0°	−1030·0°	+1030·0°	−1029·0°	+1033·0°	−1034·0°	+1056·0°	−1055·0°	+993·0°	−990·0°
Li_{4602} ..	755·0	753·0	742·0	747·0	746·0	746·0	752·0	750·0	755·0	756·0	717·0	718·0
Cd_{4678} ..	694·0	693·0	684·0	683·0	682·0	681·0	692·0	691·0	694·0	693·0	662·0	661·0
Cd_{4800} ..	612·0	610·0	603·0	601·0	602·0	600·0	609·0	607·0	610·0	608·0	582·0	584·0
Cd_{5086} ..	473·0	473·0	465·0	464·0	464·0	463·0	472·0	471·0	471·0	470·0	452·0	450·0
Ag_{5209} ..	430·0	431·0	422·0	420·0	423·0	421·0	431·0	430·0	426·0	424·0	412·0	411·0
Hg_{5461} ..	360·0	362·0	351·0	352·0	352·0	354·0	358·0	361·0	356·0	354·0	344·0	342·0
Hg_{5780} ..	296·0	297·0	288·0	288·0	289·0	290·0	294·0	296·0	290·0	291·0	281·0	281·0
Na_{5893} ..	278·0	280·0	270·0	272·0	271·0	273·0	276·0	276·0	272·0	274·0	264·0	267·0
Li_{6104} ..	249·0	248·0	241·0	244·0	244·0	245·0	246·0	247·0	245·0	246·0	236·0	237·0
Cd_{6439} ..	214·0	215·0	207·0	208·0	208·0	209·0	212·0	213·0	208·0	209·0	202·0	203·0
Li_{6708} ..	188·0	190·0	181·0	182·0	182·0	184·0	186·0	189·0	183·0	185·0	177·0	178·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE IV. *3-Nitro-4-chloroanilinomethylenecamphors*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c.c. $\{d$	0·1000		0·1000		0·1000		0·1000		0·1000		0·0500	
$\{l$	0·1000		0·1000		0·1000		0·1000		0·1000		0·0500	
Calculated $[\alpha]$	$\pm \frac{65·59}{\lambda^2-0·1268}$		$\pm \frac{65·32}{\lambda^2-0·1203}$		$\pm \frac{64·45}{\lambda^2-0·1200}$		$\pm \frac{61·69}{\lambda^2-0·1222}$		$\pm \frac{57·11}{\lambda^2-0·1201}$		$\pm \frac{54·14}{\lambda^2-0·1169}$	
Calculated λ_0	0·3561		0·3468		0·3464		0·3496		0·3465		0·3419	
Line λ	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{4800} ..	+500·0°	−495·0°	+470·0°	−475·0°	+465·0°	−465·0°	+455·0°	−450·0°	+415·0°	−415·0°	+480·0°	−470·0°
Cd_{5086} ..	455·0	455·0	435·0	430·0	425·0	425·0	415·0	410·0	380·0	380·0	390·0	380·0
Ag_{5209} ..	380·0	385·0	365·0	370·0	360·0	365·0	350·0	345·0	320·0	315·0	350·0	350·0
Hg_{5461} ..	315·0	320·0	310·0	305·0	305·0	300·0	290·0	285·0	265·0	270·0	290·0	300·0
Hg_{5780} ..	300·0	295·0	290·0	285·0	285·0	280·0	275·0	275·0	250·0	250·0	250·0	250·0
Na_{5893} ..	265·0	265·0	260·0	260·0	255·0	250·0	245·0	250·0	225·0	225·0	240·0	230·0
Li_{6104} ..	235·0	250·0	230·0	225·0	225·0	220·0	210·0	215·0	195·0	190·0	210·0	220·0
Cd_{6439} ..	200·0	210·0	195·0	205·0	190·0	195·0	185·0	185·0	175·0	175·0	190·0	180·0
Li_{6708} ..	No mutarotation		No mutarotation		Shows mutarotation; after 24 hrs. $[\alpha]^{35°\,C.}_{Hg5461}$ for $d=295·0°$ and for $l=290·0°$		No mutarotation		No mutarotation		No mutarotation	

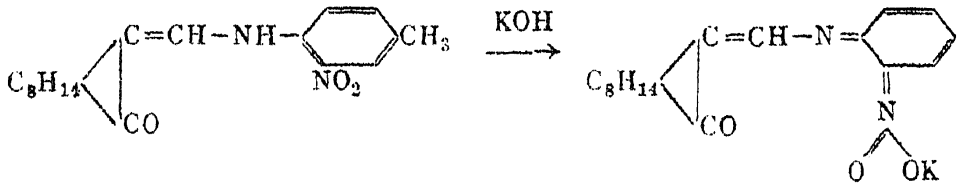
TABLE V. 2-*Nitro*-p-*toluidinomethylenecamphors*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c.c. (d / l)	0·2500 0·2500		0·2500 0·2500		0·2500 0·2500		0·2500 0·2500		0·2500 0·2500		0·1000 0·1000	
Calculated $[\alpha]$	$\pm \frac{66\cdot68}{\lambda^2-0\cdot1271}$		$\pm \frac{66\cdot21}{\lambda^2-0\cdot1215}$		$\pm \frac{65\cdot54}{\lambda^2-0\cdot1206}$		$\pm \frac{65\cdot02}{\lambda^2-0\cdot1190}$		$\pm \frac{61\cdot26}{\lambda^2-0\cdot1127}$		$\pm \frac{52\cdot39}{\lambda^2-0\cdot1201}$	
Calculated λ_0	0·3565		0·3486		0·3472		0·3450		0·3357		0·3465	
Line λ	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	l	d	l	d	l	d	l	d	l	d	l
Cd_{4800} ..	..	..	..	..	..	..	..	..	..	..	+475·0°	−470·0°
Cd_{5086} ..	+504·0°	−508·0°	+486·0°	−484·0°	+476·0°	−474·0°	..	..	+422·0°	−418·0°	375·0	375·0
Ag_{5209} ..	464·0	464·0	440·0	442·0	436·0	436·0	+430·0°	−426·0°	390·0	388·0	345·0	350·0
Hg_{5461} ..	388·0	386·0	376·0	374·0	368·0	368·0	362·0	364·0	330·0	332·0	295·0	290·0
Hg_{5780} ..	324·0	322·0	314·0	312·0	308·0	306·0	304·0	302·0	278·0	276·0	245·0	245·0
Na_{5893} ..	302·0	302·0	292·0	290·0	290·0	288·0	288·0	286·0	264·0	264·0	230·0	235·0
Li_{6104} ..	268·0	270·0	266·0	262·0	258·0	260·0	254·0	254·0	2[illegible]·0	238·0	205·0	210·0
Cd_{6439} ..	236·0	234·0	228·0	230·0	226·0	226·0	222·0	224·0	200·0	204·0	180·0	175·0
Li_{6708} ..	210·0	210·0	200·0	202·0	198·0	200·0	196·0	198·0	178·0	180·0	160·0	155·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE VI. *4-Nitro-o-toluidinomethylenecamphors*

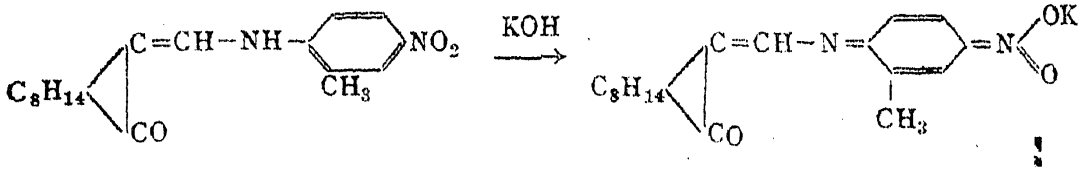
Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentratration in gm./100 c.c.	*d* 0·5000	*l* 0·5000	0·5000	0·5000	0·5000	0·5000	0·5000	0·5000	0·5000	0·5000	0·5000	0·5000
Calculated $[\alpha]_{\lambda_0}$	$\pm \frac{57\cdot16}{\lambda^2-0\cdot1342}$ 0·3664		$\pm \frac{57\cdot8}{\lambda^2-0\cdot1339}$ 0·3659		$\pm \frac{58\cdot58}{\lambda^2-0\cdot1329}$ 0·3645		$\pm \frac{58\cdot03}{\lambda^2-0\cdot1420}$ 0·3768		$\pm \frac{56\cdot38}{\lambda^2-0\cdot1381}$ 0·3716		$\pm \frac{55\cdot24}{\lambda^2-0\cdot1342}$ 0·3664	
Line λ	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*e*	*d*	*l*
Cd_{5086} ..	..	..	+461·0°	−464·0°	+461·0°	−464·0°	..	..	+471·0°	−467·0°	+445·0°	−443·0°
Ag_{5209} ..	+416·0°	−418·0°	420·0	419·0	421·0	423·0	+449·0°	−450·0°	422·0	424·0	404·0	4 2·0
Hg_{5461} ..	350·0	348·0	352·0	353·0	355·0	354·0	370·0	371·0	353·0	352·0	339·0	338·0
Hg_{5780} ..	285·0	284·0	289·0	288·0	293·0	292·0	302·0	303·0	287·0	287·0	276·0	276·0
Na_{5893} ..	269·0	270·0	273·0	272·0	272·0	273·0	231·0	284·0	268·0	270·0	260·0	258·0
Li_{6104} ..	240·0	240·0	242·0	243·0	245·0	247·0	253·0	250·0	241·0	239·0	233·0	231·0
Cd_{6439} ..	203·0	202·0	206·0	205·0	209·0	210·0	215·0	212·0	204·0	201·0	196·0	199·0
Li_{6708} ..	181·0	179·0	183·0	182·0	183·0	186·0	187·0	189·0	179·0	182·0	174·0	176·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

Table II), whereas no such deepening of colour is observed in the case of the *meta*-nitro compounds (III and IV, Table II). This is due to the fact that *ortho*- and *para*-nitro derivatives can change in alkaline solution into the *aci*-form having quinonoid structure as illustrated in the following formulæ:



3-Nitro-*p*-toluidinomethylenecamphor (VI, Table II); yellow-orange in alcohol

2 conjugate double bonds (shortest route)
4 conjugate double bonds (longest route)
Port-wine red

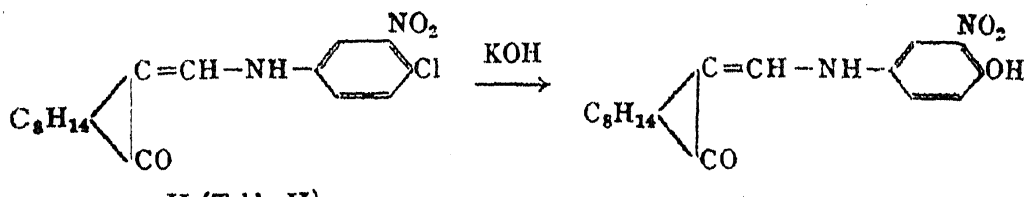


5-Nitro-*o*-toluidinomethylenecamphor (VII, Table II); yellow in alcohol

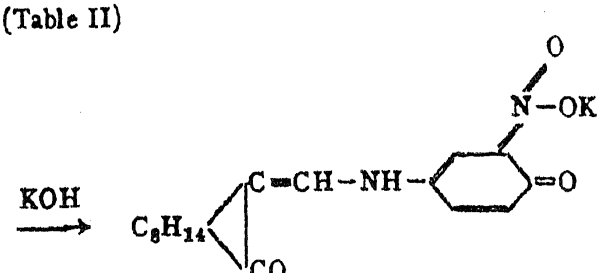
3 conjugate double bonds (either route)
Deep violet

Further, the chain of conjugate double bonds is longer in the *para*-quinonoid structure than that in the *ortho*-quinonoid structure; this explains the deeper colour of the *para*-nitro compound than that of the *ortho*-nitro compound.

The abovementioned tautomerisation to the *aci*-quinonoid form is not possible in the case of the *meta*-nitro compounds (III and IV, Table II); therefore, there is no change in colour when their alcoholic solution is made alkaline. The port-wine red colour of 3-nitro-4-chloroanilinomethylene-camphor (II, Table II), a *meta*-nitro derivative, in alkaline solution can, however, be explained by assuming that the Cl atom, which is rendered labile by the adjacent NO_2 group, is replaced by the hydroxyl group, thus permitting tautomerisation into the *ortho*-quinonoid structure:



II (Table II)



Our results are thus in agreement with the modern views of the influence of chemical constitution on colour.[4]

Dyeing Properties of Compounds II, III, IV and VI (Table II)

These substances, being acid dyes, have been examined for their dyeing properties on wool from an acid-bath containing 2% sulphuric acid and 10% Glauber's salt: 3-nitro-*p*-toluidinomethylenecamphor (VI) dyes wool a light yellow-orange colour which is fast to washing with soap and to sunlight (30 hours' exposure); 3-nitro-4-chloroanilinomethylenecamphor (II), 2-nitro-*p*-toluidinomethylenecamphor (III) and 4-nitro-*o*-toluidinomethylenecamphor (IV) dye wool light yellow colour which is fast to washing with soap. Sunlight, however, causes fading in these colours to a slight extent after a moderate exposure (12 hours).

Experimental

General Method of Preparation.—The *dextro*-forms of the compounds were prepared by adding oxymethylene-*d*-camphor (1 mol. proportion), dissolved in ethyl alcohol, to the solution of the free base in acetic acid, when a precipitate was obtained immediately or on keeping. It was then repeatedly recrystallised from ethyl alcohol.

The *lævo*- and *racemic*-isomers were prepared in the same way as the corresponding *dextro*-compounds and had similar crystalline form and solubility.

2 : 5-*Dichloroanilinomethylene*-d-*camphor*, m.p. 139–140° C., was obtained as crystals with yellow tinge. It is very soluble in acetone, pyridine, chloroform and benzene, less so in methyl and ethyl alcohols, and insoluble in water. (Found: Cl, 21·89; N, 4·05. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87; N, 4·32 per cent.)

2 : 5-*Dichloroanilinomethylene*-l-*camphor*, m.p. 139–140° C. (Found: Cl, 21·92. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87 per cent.)

2 : 5-*Dichloroanilinomethylene*-dl-*camphor*, m.p. 136·5–137·5° C. (Found: Cl, 21·87. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-d-*camphor*, m.p. 215–216° C., was obtained as bright yellow rectangular plates. It is soluble in pyridine, less so in acetone, sparingly soluble in chloroform and methyl and ethyl alcohols, very sparingly soluble in benzene, and insoluble in water. (Found: Cl, 10·80; N, 8·19. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59; N, 8·37 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-l-*camphor*, m.p. 215–216° C. (Found: Cl, 10·77. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-dl-*camphor*, m.p. 204–205° C. (Found: Cl, 10·79. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59 per cent.)

2-*Nitro*-p-*toluidinomethylene*-d-*camphor*, m.p. 193–194° C., was obtained as long lemon-yellow rectangular plates. It is soluble in pyridine, moderately soluble in acetone, chloroform and methyl and ethyl alcohols, sparingly soluble in benzene, and insoluble in water. (Found: N, 8·73. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

2-*Nitro*-p-*toluidinomethylene*-l-*camphor*, m.p. 193–194° C. (Found: N, 8·75. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

2-*Nitro*-p-*toluidinomethylene*-dl-*camphor*, m.p. 181–182° C. (Found: N, 8·72. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

4-*Nitro*-o-*toluidinomethylene*-d-*camphor*, m.p. 137·5–138·5° C., was obtained as lemon-yellow needles. It is very soluble in pyridine, chloroform, acetone and benzene, less so in methyl and ethyl alcohols, and insoluble in water. (Found: N, 8·71. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

4-*Nitro*-o-*toluidinomethylene*-l-*camphor*, m.p. 137·5–138·5° C. (Found: N, 8·73. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

4-*Nitro*-o-*toluidinomethylene*-dl-*camphor*, m.p. 139–140° C. (Found : N, 8·74. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

The rotatory power determinations were carried out in a 2-dcm. jacketed tube at 35° C. 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

1. The rotatory dispersion of optically active forms of 2:5-dichloroanilino-, 3-nitro-4-chloroanilino-, 2-nitro-*p*-toluidino- and 4-nitro-*o*-toluidinomethylenecamphors has been investigated in six solvents for the visible spectrum (λ_{6708} to λ_{4358}), and found to obey the Drude's one-term equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$; it is therefore simple.

2. Within the limits of experimental error the *d*- and *l*-forms of these compounds possess identical rotatory power.

3. The effect of the polarities (as deduced from specific inductive capacity) of Cl, CH_3 and NO_2 groups on the rotatory power has been studied. With minor deviations, Cl and CH_3 groups, being negative, lower the rotatory power, whereas NO_2 group, being positive, raises the rotatory power. Thus the polar effect of substituent groups is traceable in optical activity.

4. Subject to minor deviations, the sequence (decreasing or increasing) of the rotatory power of these compounds runs parallel with that of the dielectric constants of the solvents in which the rotatory power is determined.

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