CCXXV.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part IV. Aryl Derivatives of Bisiminocamphor.*

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THE remarkably high molecular rotatory power displayed by products of condensing camphorquinone with aryldiamines was first noticed in connexion with *p*-phenylenebisiminocamphor (Forster and Thornley, T., 1909, **95**, 941). The rotation of this compound is greatly exceeded by that of 1 : 4-naphthylenebisiminocamphor (B. K. Singh and M. Singh, T., 1920, **117**, 1599), and we now find that the molecular rotatory power of *pp'*-bisiminocamphor-

diphenylamine, prepared from camphorquinone and *pp'*-diaminodiphenylamine, is even greater, as indicated below :

	[M] _D .			
	Chloroform.	Methyl alcohol.	Ethyl alcohol.	Pyridine.
<i>pp'</i> -Bisiminocamphordiphenylamine	11385°	12375°	14231°	13288°
1 : 4-Naphthylenebisiminocamphor	8175	9052	12071	13416
<i>p</i> -Phenylenebisiminocamphor	6088	5009	5289	6173

The conventional formula for *pp'*-bisiminocamphordiphenylamine, in which the continuity of conjugated linkings is broken, suggests

an exception to the generalisation which has arisen from the study of such substances, namely, exaltation of rotatory power following concentration of conjugated linkings, azethenoid groups and benzene rings within a narrow molecular compass (Forster and Spinner, T., 1919, **115**, 889; B. K. Singh and M. Singh, *loc. cit.*). A similar anomaly is presented by camphorylamino phenyliminocamphor (Forster and Saville, this vol., p. 789), the molecular rotatory power of which exceeds that of *p*-phenylenebisiminocamphor. The case of *pp'*-bisiminocamphordiphenylamine, however, can be brought into harmony with the above generalisation by representing one of the benzene rings in the quinonoid form capable of displaying double symmetric tautomerism,

the continuity of the conjugated linkings thus becoming restored. The fluorescence to be expected from such a compound is, in this case, weak, but a hydroxyl group is indicated by the greenish-red coloration with ferric chloride.

pp'-Bisiminocamphordiphenylamine is interesting also as a rare example of optically active dyes. Furthermore, it is phototropic and thermotropic, the yellow form changing to brown in sunlight; although the converse change does not occur in darkness, the brown modification rapidly becomes yellow above 75°. The remaining new compounds described in this paper, namely, *oo'*-ditolylene-

bisiminocamphor, *oo'*-dimethoxydiphenylenebisiminocamphor, and *pp'*-diphenylenebisaminocamphor, are in agreement with the above-mentioned generalisation; the first-named resembles *pp'*-diphenylenebisiminocamphor (Forster and Spinner, *loc. cit.*) in being dimorphous, but, unlike the authors quoted, we have reduced the latter substance to *pp'*-diphenylenebisaminocamphor. The effect of ortho-substitution on the rotatory power of *pp'*-diphenylenebisiminocamphor is very depressant, as indicated by the following measurements :

	[M] _D .	
	Chloroform.	Methyl alcohol.
<i>pp'</i> -Diphenylenebisiminocamphor :		
(a) Yellowish-green	5472°	—
(b) Golden-brown	5433	5020°
<i>oo'</i> -Ditolylenebisiminocamphor :		
(a) Green	3929	3274
(b) Golden-yellow	4007	3462
<i>oo'</i> -Dimethoxydiphenylenebisiminocamphor ...	2003	1576

Thus the sequence of substituents in order of diminishing rotatory power is $H > CH_3 > OCH_3$.

EXPERIMENTAL.

Camphorquinone (3.3 grams), tolidine dihydrochloride (2.85 grams), and excess of fused sodium acetate having been heated on the water-bath during four hours, the hard mass was extracted with 10 c.c. of cold alcohol, and the residue undissolved by water was crystallised fractionally from ether. The less soluble, preponderating component (*a*), which separated in long, green prisms, melts at 200—201°, and is readily soluble in chloroform, acetone, or hot ethyl alcohol, less so in methyl alcohol or ether; it is insoluble in cold ethyl alcohol or water (Found: N = 5.2. $C_{34}H_{40}O_2N_2$ requires N = 5.5 per cent.). The more soluble form (*b*), in golden-yellow prisms, melts at 198—199°, and is readily soluble in chloroform or acetone, less so in hot ethyl alcohol, and even more insoluble in hot methyl alcohol (Found: N = 5.2 per cent.). A mixture of *a* and *b* in equal amounts melts at 192—193°.

The following measurements of rotatory power, in common with all noted in this paper, are recorded as relating to the specified weight of material in 100 c.c. observed in a 2-dcm. tube, the initial reading having been taken within half-an-hour :

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Solvent.	Gr./100 c.c.	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.1280 (a)	29°	1.98°	773°	3929°
Methyl alcohol	0.1148 (a)	30	1.48	645	3274
Chloroform	0.0564 (b)	29	0.89	789	4007
Acetone	0.2708 (b)	21	3.98	736	3736
Methyl alcohol	0.0834 (b)	29	1.14	683	3470

The foregoing rotations remained unchanged during twenty-four hours.

Camphorquinone (3.3 grams), dianisidine dihydrochloride (3.9 grams), and excess of sodium acetate having been heated on the water-bath during four hours, the residue undissolved by 10 c.c. of cold alcohol followed by water was crystallised from hot alcohol, which deposited thin, green prisms melting at 186° (Found: N = 4.84. $C_{34}H_{40}O_4N_2$ requires N = 5.18 per cent.). The substance dissolves very readily in chloroform or ether, less so in methyl alcohol and hot ethyl alcohol; it does not display mutarotation:

Solvent.	Gr./100 c.c.	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.1670	22°	1.24°	371°	2003°
Methyl alcohol	0.2635	„	1.53	290	1567

The *pp'*-diphenylenebisiminocamphor required in preparing the above product of reduction was divided into the less soluble component (a), which separated in yellowish-green prisms melting at 276°, and the more soluble component (b), forming golden-brown needles which melt at 274°, as described by Forster and Spinner (*loc. cit.*); a mixture of a and b in equal amounts melts at 267°. The substance does not display mutarotation:

Solvent.	Gr./100 c.c.	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.2570 (a)	35°	5.86°	1140°	5472°
„	0.4730 (b)	„	10.71	1132	5433
Methyl alcohol ...	0.0908 (b)	29	1.90	1046	5020

pp'-Diphenylenebisaminocamphor was produced from both modifications on agitating ethereal solutions with zinc dust and 10 per

cent. aqueous potassium hydroxide during six hours, the residue from evaporating the colourless solution being crystallised from hot alcohol, which deposited plates on cooling. The product from each source, and a mixture thereof, melted at 214° (Found: C = 79.4; H = 8.28. $C_{32}H_{40}O_2N_2$ requires C = 79.3; H = 8.27 per cent.). It is insoluble in water, but dissolves readily in chloroform or acetone; less so in methyl or ethyl alcohol.

Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.2920	17°	0.57°	97.6°	472°
Methyl alcohol	0.0650	„	0.10	76.9	372
Acetone.....	0.1435	„	0.47	163.7	792

The substance, either solid or dissolved, becomes yellow in sunlight and remains in this form when left in darkness; the above solution in acetone, after six hours in sunlight, gave $[\alpha]_D 282^{\circ}$, whence $[M]_D 1365^{\circ}$, unchanged after twelve hours in darkness.

pp'-Bisiminocamphordiphenylamine (I or II).

Camphorquinone (1.66 grams), *pp'*-diaminodiphenylamine (1 gram), and fused sodium acetate were heated on the water-bath during two hours, the product being extracted with absolute alcohol, precipitated by water, and redissolved in hot alcohol, from which the substance crystallised (Found: N = 8.06. $C_{32}H_{37}O_2N_3$ requires N = 8.48 per cent.). It forms yellow prisms melting at 210 – 212° , and is insoluble in water, but dissolves in chloroform, benzene, or methyl alcohol, and less readily in ethyl alcohol. The alcoholic solution develops a greenish-red coloration with ferric chloride, and a deep, but transient, cherry red with mineral acids, becoming yellow with alkalis and returning with acids. It dyes wool yellow with alum, and somewhat deeper with chrome in an alcoholic bath of 2 per cent. The fluorescence in organic solvents is a feeble green, and there is no mutarotation:

Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.1300	23°	5.98°	2300°	11385°
„ (brown form)...	0.0364	30	1.72	2370	11731
Methyl alcohol	0.0554	23	2.77	2500	12375
Acetone	0.0376	19	1.99	2646	13097
Ethyl alcohol	0.0440	„	2.53	2875	14231
Pyridine	0.1084	30	5.82	2685	13288

Exposure to sunlight during a few minutes converts the substance into a brown modification which does not revert in darkness, but becomes yellow when heated above 75° . The two forms and their

mixture melt at the same temperature and have the same rotatory power.

For comparison with aryl derivatives of bisiminocamphor the parent substance, azocamphanone, was examined in the polarimeter (compare Forster and Zimmerli, T., 1910, 97, 2165) :

Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.2605	30°	0.98°	188°	616°
Methyl alcohol	0.1660	„	0.76	229	750

Hydrochlorides of Bases in Condensation.

Free tolidine and dianisidine do not undergo condensation with camphorquinone even at high temperatures (120—125°) and with prolonged heating alone, or with sodium sulphate or zinc chloride. Action proceeds readily with the hydrochlorides, however, and benzidine combines in either form (compare G. M. Robinson and R. Robinson, T., 1918, 113, 644).

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