674. *The Rotatory Dispersion and Circular Dichroism of* (−)-2-*Chloro-2-nitrosocamphane and the Pyridine Salt of* (+)-2-*Chloro-2-nitroso-camphane-10-sulphonic Acid.*

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Continuing our search for substances suitable for asymmetric photolysis, we have prepared two new chloro-nitroso-terpene derivatives which show the Cotton effect.

For (−)-2-chloro-2-nitrosocamphane (in alcohol) $[a]_{6000} = +964°$, $[a]_{7100} = -946°$, and the anisotropy factor (g) reaches -0.15 at 7200 A. When in solution the compound is stable if kept in the dark, but irradiation with red light causes inversion of the rotatory dispersion curve. The pyridine salt of (+)-2-chloro-2-nitrosocamphane-10-sulphonic acid does not mutarotate in this way. In methyl alcohol it has $[a]_{6550} = +805°$, $[a]_{5600} = -636°$, and $g = +0.07$ at 6250 A.

NITROSO-COMPOUNDS, in which the nitroso-group is attached to an asymmetric carbon atom, exhibit the Cotton effect when present in solution as simple molecules. Chloro-nitroso-compounds of the type $R \cdot CR'Cl \cdot NO$ are always unimolecular, and one of them (in which $R = Ph \cdot CH_2$ and $R' = CH_2 \cdot CH_2 \cdot CO_2H$) has recently been resolved by Mitchell and Naismith (*J.*, 1949, 3116). The anisotropy factor was smaller, however, than that obtained by Mitchell and Cormack (*J.*, 1932, 1415) for bornylene nitrosite (a white bimolecular compound which gives blue solutions on warming) and it was thought that if some chloro-nitroso-terpenes could be prepared they might furnish interesting examples of the Cotton effect.

TABLE I.

Rotatory dispersion of (−)-2-*chloro-2-nitrosocamphane in alcohol.*

$c = 0.280$ g./100 ml.; $l = 1$ dm.; $t = 18°$.

λ	5000	5200	5400	5500	5600	5700	5800	5900	6000	6100	6200
α	+1·32°	+1·44°	+1·60°	+1·80 °	+1·92°	+2·16°	+2·45°	+2·65°	+2·70°	+2·65°	+2·60°
[a]	+471°	+514°	+571°	+643°	+686°	+771°	+875°	+946°	+964°	+946°	+929°

λ	6300	6400	6500	6600	6700	6800	6900	7000	7100	7200
α	+2·65°	+2·60°	+2·15°	+0·95°	−0·05°	−1·75°	−2·25°	−2·55°	−2·65°	−2·45°
[a]	+946°	+929°	+768°	+339°	−179°	−625°	−804°	−911°	−946°	−875°

TABLE II.

Circular dichroism and absorption of (−)-2-*chloro-2-nitrosocamphane in alcohol.*

For $ε_l − ε_r$, concn. $= 0.0141$M., $l = 2.5$ cm.; and for $ε$, concn. $= 0.0680$M., $l = 1$ cm.

λ.	$ε_l − ε_r$.	$ε$.	g.	λ.	$ε_l − ε_r$.	$ε$.	g.
5400	—	1·68	—	6500	−0·85	12·50	−0·068
5600	—	2·65	—	6550	−0·94	12·90	−0·073
5700	−0·08	3·25	−0·025	6600	−1·08	12·90	−0·084
5800	−0·10	4·15	−0·024	6650	−1·14	12·50	−0·091
5900	−0·19	5·30	−0·036	6700	−1·14	11·60	−0·098
6000	−0·30	6·45	−0·047	6800	−1·06	8·90	−0·119
6100	−0·36	7·65	−0·047	6900	−0·85	6·20	−0·137
6200	−0·47	8·70	−0·054	7000	−0·55	4·10	−0·134
6300	−0·57	9·65	−0·059	7100	−0·37	2·60	−0·142
6400	−0·64	11·50	−0·056	7200	−0·27	1·80	−0·150

Following the procedure of Mitchell and Dawson (*J.*, 1944, 452), we dissolved camphor oxime in dry ether and passed in chlorine. The solution became blue and then green, and the oxime hydrochloride which separated was filtered off. Removal of the ether gave a blue solid which showed the Cotton effect (in alcohol) with a rotation maximum at about 6000 A.,

but $[\alpha]_{6000}$ varied between $+100°$ and $+200°$ in different preparations. When the oxime hydrochloride was used (instead of the oxime) in a large excess of ether, the resulting product had $[\alpha]_{6000} \simeq 700°$, and chromatographic treatment finally raised it to 964°. We concluded that the compound was 2-chloro-2-nitrosocamphane because of (a) the method of preparation, (b) the blue colour, (c) the analysis which agreed with $C_{10}H_{16}ONCl$, and (d) the product of photo-oxidation ($C_{10}H_{16}O_2NCl$) which closely resembled the chloronitrocamphane prepared by Forster (J., 1900, **77**, 263) by acting on camphor oxime with a solution of sodium hypochlorite.

Rotation and circular dichroism readings were taken for a number of wave-lengths with the apparatus described by Mitchell and Simpson (J., 1940, 784), and absorption data were obtained with a Unicam spectrophotometer. The results are set out in Tables I and II.

During the work on rotatory dispersion, it was observed that solutions of (−)-2-chloro-2-nitrosocamphane are abnormally sensitive to red light (in the absence of oxygen), so the following experiment was carried out. An alcoholic solution of the compound (0·030 g./10 ml.), in a 1-cm. cell closed with a ground stopper, was exposed to light (from a 1000 c.p. Pointolite lamp) which had passed through a condensing lens, a circulating water filter, and a piece of red glass. Table III gives α_{6000} after the periods of irradiation stated :

TABLE III.

Mins.	0	15	30	60	75	105	165	225	495	660
α_{6000}	$+2·30°$	$+0·98°$	$+0·13°$	$−0·30°$	$−0·51°$	$−0·84°$	$−0·88°$	$−0·81°$	$−0·70°$	$−0·61°$

It is evident from these results that two processes are going on simultaneously—(1) fairly rapid mutarotation and (2) slow photolysis. This is the first case of photochemical mutarotation among chloronitroso-compounds, but they all undergo photolysis on exposure to red light. Fig. 1 shows the rotatory dispersion at the beginning (curve 1) and after 15, 30, and 165 minutes of irradiation (curves 2, 3, and 4). An inversion of the original Cotton effect has thus been produced. The mechanism underlying this inversion is of some importance and is being investigated further.

FIG. 1.
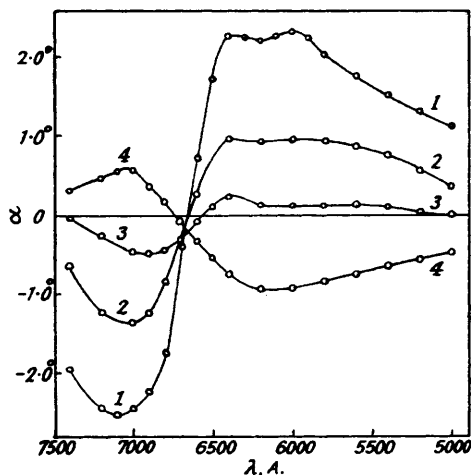
From the standpoint of asymmetric photolysis, the most encouraging feature of (−)-2-chloro-2-nitrosocamphane is the large anisotropy factor and the mutarotation is an unfortunate complication. It was thought that a more stable molecule might be obtained if instead of camphor we used camphor-10-sulphonic acid as starting material. Its oxime did not dissolve in ether so we tried pyridine as solvent, and this led to the isolation of the pyridine salt of (+)-2-chloro-2-nitrosocamphane-10-sulphonic acid. After three crystallisations from alcohol, the rotation (at 6000 A.) and the melting point became constant. No mutarotation was observed when solutions of this compound were irradiated with red light. Rotatory dispersion, circular dichroism, and absorption readings were taken (in methyl alcohol) and are shown in Tables IV and V.

TABLE IV.

Rotatory dispersion of the pyridine salt of (+)-2-chloro-2-nitrosocamphane-10-sulphonic acid in methyl alcohol.

$c = 0.220$ g./100 ml.; $l = 1$ dm.; $t = 18°$.

λ	4750	5000	5200	5400	5500	5600	5700	5800	5900	6000	6100
a	−0·65°	−0·76°	−0·96°	−1·20°	−1·35°	−1·40°	−1·35°	−1·15°	−1·00°	−0·90°	−0·58°
[a]	−295°	−345°	−436°	−546°	−614°	−636°	−614°	−523°	−455°	−409°	−264°

λ	6200	6300	6400	6500	6550	6600	6800	6900	7000	7200
a	−0·20°	+0·85°	+1·50°	+1·75°	+1·77°	+1·70°	+1·20°	+0·95°	+0·80°	+0·60°
[a]	−91°	+386°	+682°	+795°	+805°	+773°	+546°	+432°	+364°	+273°

TABLE V.

Circular dichroism and absorption of the pyridine salt of (+)-2-chloro-2-nitrosocamphane-10-sulphonic acid in methyl alcohol.

For $\varepsilon_l - \varepsilon_r$, concn. $= 0.0151$M., $l = 2.5$ cm.; and for ε, concn. $= 0.0230$M., $l = 1$ cm.

| λ.	$\varepsilon_l - \varepsilon_r$.	ε.	g.	λ.	$\varepsilon_l - \varepsilon_r$.	ε.	g.
5200	0·08	2·30	0·035	6200	1·21	18·50	0·065
5400	0·15	3·90	0·038	6250	1·27	19·20	0·066
5500	0·21	5·10	0·041	6300	1·21	19·40	0·062
5600	0·30	6·70	0·045	6350	1·14	18·80	0·061
5700	0·49	9·20	0·053	6400	1·05	17·30	0·061
5800	0·64	10·80	0·059	6500	0·71	12·80	0·055
5900	0·70	11·80	0·059	6600	0·49	8·30	0·059
6000	0·86	13·80	0·062	6700	0·26	5·20	0·050
6100	1·05	16·20	0·065	6800	0·08	3·30	0·024
6150	1·14	17·80	0·064	6900	0·04	2·00	0·020

FIG. 2.
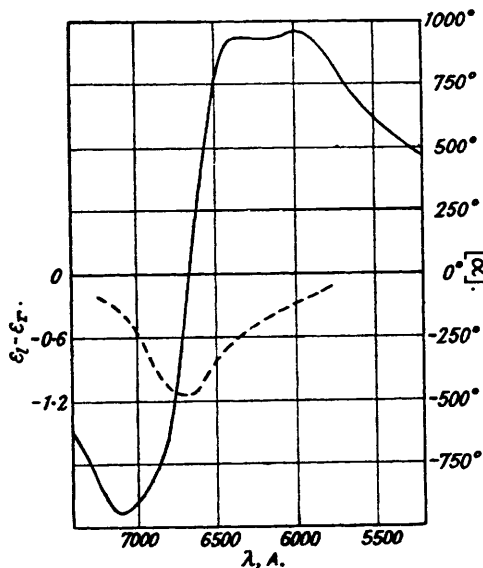
FIG. 3.
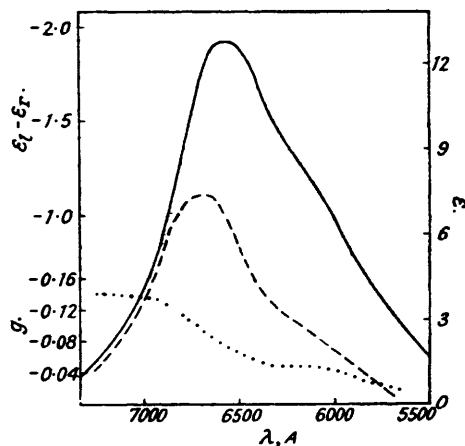
Discussion of the Results.—The data for (−)-2-chloro-2-nitrosocamphane are given graphically in Figs. 2 and 3, and those for the pyridine salt of (+)-2-chloro-2-nitrosocamphane-10-sulphonic acid in Figs. 4 and 5. Rotatory dispersion curves (full line) and circular dichroism curves (broken line) are given in Figs. 2 and 4, while curves of absorption (full line), circular dichroism (broken line), and anisotropy factors (dotted line) are contained in Figs. 3 and 5. To make Fig. 3 more compact and to facilitate comparison with Fig. 5 we have plotted negative values of $\varepsilon_l - \varepsilon_r$ and of g upwards.

For (−)-2-chloro-2-nitrosocamphane (Fig. 2) the rotatory dispersion curve crosses the axis of zero rotation at about the same wave-length ($\simeq 6700$ A.) as the circular dichroism curve passes through its negative maximum, but in Fig. 3 the maxima of circular dichroism and

absorption do not coincide (ε_{max}. being situated at about 6550 A.). This has a considerable effect on the anisotropy factor (g) which reaches −0·15 on the long-wave side of the absorption band. Somewhat similar results were obtained for camphor by Kuhn and Gore (*Z. physikal. Chem.*, 1931, *B*, **12**, 389) and for camphorsulphonic acid by Lowry and French (*J.*, 1932, 2645).

With the pyridine salt of (+)-2-chloro-2-nitrosocamphane-10-sulphonic acid (Figs. 4 and 5) the Cotton effect is inverted, and ($\varepsilon_l - \varepsilon_r)_{max}$, ε_{max}, and g_{max} are all situated near 6250 A. where $[\alpha] \simeq 0$. This partly explains why g_{max} has a smaller value (0·07) than in Fig. 3. Another reason is the increase in ε_{max}. (from 12·9 in Fig. 3 to 19·4 in Fig. 5).
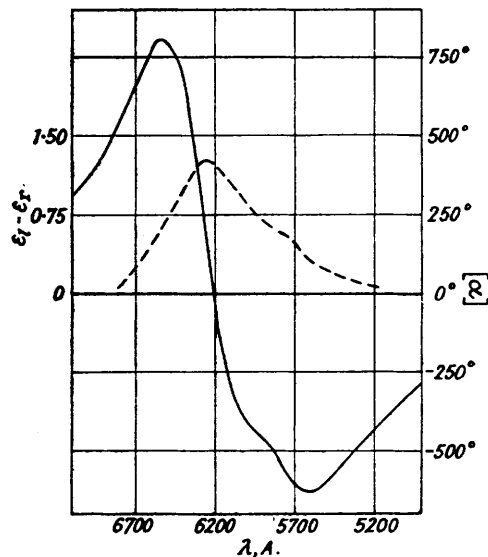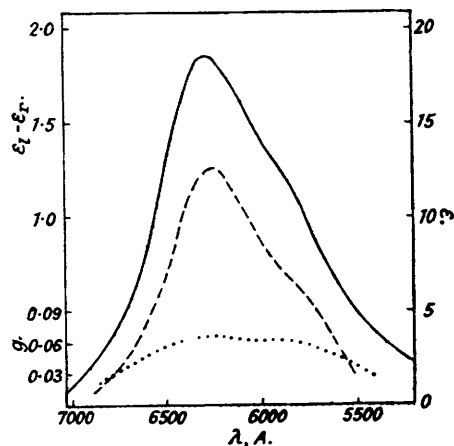
FIG. 4.

FIG. 5.

EXPERIMENTAL.

Camphor Oxime Hydrochloride.—The oxime of (+)-camphor was obtained essentially as described by Auwers (*Ber.*, 1889, **22**, 605) and had m. p. 118°. The hydrochloride was prepared by passing dry hydrogen chloride into a solution of the oxime in dry ether cooled to 0°. The precipitated hydrochloride was filtered off, and after crystallisation from alcohol had m. p. 160°.

(−)-2-*Chloro-2-nitrosocamphane.*—A solution of 1 g. of camphor oxime hydrochloride in 500 ml. of dry ether was cooled in ice, and dry chlorine led in until the solution had become dark green (about 2 hours). On removal of the ether, the remaining blue solid was crystallised from methyl alcohol. A 5% solution of the crystals ($[\alpha]_{6000} \simeq 700°$) was passed through an alumina column (60 cm. long and 1 cm. in diameter) and gave a product which after further crystallisation from methyl alcohol had m. p. 127° (decomp.) and $[\alpha]_{6000} = 964°$ (Found : C, 59·6; H, 7·6; N, 6·9. $C_{10}H_{16}ONCl$ requires C, 59·7; H, 7·9; N, 6·9%). For this preparation it is necessary to carry out all the operations in subdued light.

Photo-oxidation of (−)-2-*Chloro-2-nitrosocamphane.*—When a solution of the chloronitroso-compound (0·2770 g. in 10 ml. alcohol), in a cell attached to a gas burette containing oxygen, was irradiated with red light, 15·57 ml. of the gas were absorbed (at N.T.P.), and the blue solution became colourless. For conversion into the chloronitro-compound 15·39 ml. are required. A white crystalline substance (m. p. 217°) was recovered from the solution (Found : C, 55·3; H, 7·6. Calc. for $C_{10}H_{16}O_2NCl$: C, 55·3; H, 7·4%).

Pyridine Salt of (+)-2-*Chloro-2-nitrosocamphane-10-sulphonic Acid.*—The oxime of (+)-camphor-10-sulphonic acid was prepared as described by Reychler (*Bull. Soc. chim.*, 1898, **19**, [iii], 125) and had m. p. 180°. 4 G., dissolved in 10 ml. of pure pyridine, were cooled to −10° and chlorine was passed slowly into the solution until a deep blue-green colour had developed. The resulting semi-solid mass was filtered, leaving a blue *salt* which was washed with ether and dried on porous plate. On crystallisation from alcohol, it had m. p. 150° and, after three further crystallisations from the same solvent, the long blue needles melted at 155° (Found : C, 49·9; H, 5·8; N, 7·9. $C_{15}H_{21}O_4N_2ClS$ requires C, 49·9; H, 5·8; N, 7·8%).

(+)-2-Chloro-2-nitrosocamphane-10-sulphonic acid was obtained from its pyridine salt by addition of cold concentrated hydrochloric acid. It was difficult to purify, however, as it did not crystallise well from any of the ordinary solvents.

The microanalyses were carried out by Mr. J. M. L. Cameron and Miss R. H. Kennaway.