Rotatory Dispersion of Configurationally Related Unsaturated Secondary Carbinols and Their Corresponding Chlorides

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In several instances a periodic change in sign of the partial rotation of the chromophoric groups has been observed with the increase in the distance of these groups from the asymmetric carbon atom. In many unsaturated substances, the ethylenic bond is known to possess a partial rotation of significant value. It was desired to determine whether this partial rotation is subject to a periodic change in sign with the progressive increase in the distance of the double bond from the asymmetric center. The observations reported here seem to indicate that such a change exists although it is expressed less strikingly than in the case of the carbonyl group previously discussed.

WORK previously reported from this laboratory[1] has brought out the fact that in configurationally related substances the partial rotation of a definite absorption band of a functional group (or of a group with distinct chromophoric properties), may change its sign with the change in the distance of the group from the asymmetric center by one $-CH_2$ radical. The most striking illustration of this phenomenon is presented in the series of configurationally-related aldehydes of the general type
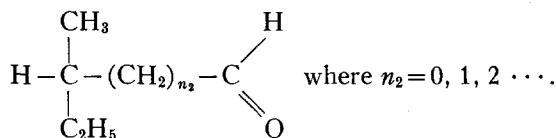
$$H-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-(CH_2)_{n_2}-C\overset{H}{\underset{O}{\big\backslash\!\!\big\backslash}} \quad \text{where } n_2 = 0, 1, 2 \cdots.$$

In this group of substances, the absorption band at $\lambda2950$ is strongly anisotropic, but the circular dichroism is of opposite sign in the first two members of the series homologous with respect to n_2 ($n_2 = 0$ and $n_2 = 1$).

Aliphatic unsaturated carbinols with one double bond represent a series in a sense similar to that of the aldehydes, inasmuch as the group with the ethylenic linkage has a distinct absorption band absent in each of the remaining three substituents on the asymmetric carbon atom. Hence it was desired to ascertain whether the effect of distance of the ethylenic bond from the

TABLE I. *Maximum rotations $[M]^{25}_{5780}$ of unsaturated and saturated configurationally related substances in homogeneous state.*

CH₂ ‖ CH | H...C...OH | C₄H₉	CH₂ ‖ CH | H...C...OH | C₅H₁₁	CH₃ | CH₂ | CH | H...C...OH | CH₃	CH₂ ‖ CH | CH₂ | H...C...OH | CH₃
$-28.1°$	$-33.3°$	$-0.35°$	$-4.9°$
Chloride $= -18°$ | C₂H₅ | H...C...OH | C₄H₉	Chloride $= -34°$ | C₂H₅ | H...C...OH | C₅H₁₁	Chloride $= -13°$ | C₃H₇ | H...C...OH | CH₃	Chloride $= -20°$ | C₃H₇ | H...C...OH | CH₃
$+9.8°$	$+11.1°$	$-12.5°$	$-12.5°$
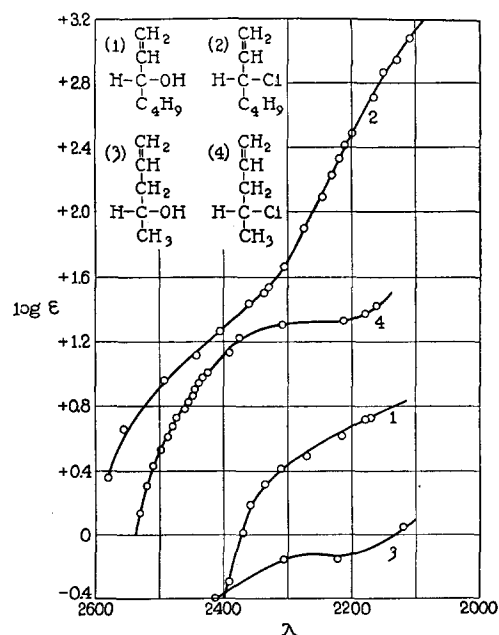
FIG. 1. Absorption curves of some unsaturated substances.

[1] P. A. Levene and A. Rothen, J. Chem. Phys. **4**, 48 (1936).

TABLE II. *Rotatory dispersion of levo-1-hepten-3-ol (vinylbutyl carbinol) and the corresponding levo-3-chloroheptene-1 and levo-3-bromoheptene-1 in homogeneous state.*

CARBINOL			CHLORIDE			BROMIDE	
Constants of sample: $d_4^{20}=0.8315$, $d_4^{25}=0.8356$ (in vacuum), $n_D^{25}=1.4313$ Visible region: $l=20$ cm U.V. region: $l=5$ cm from $\lambda3840$ to $\lambda2599$, 0.1 cm from $\lambda2440$ to $\lambda2384$, 0.05 cm for $\lambda2340$ $[M]^{25}_{max}=-\dfrac{23.2830}{\lambda^2-0.0365}+\dfrac{15.7476}{\lambda^2-0.020}$			Constants of sample: $d_4^{25}=0.8883$ (in vacuum), $n_D^{25}=1.4380$ Visigle region: $l=20$ cm U.V. region: $l=5$ cm from $\lambda3830$ to $\lambda2960$, 1 cm from $\lambda2920$ to $\lambda2775$, 0.1 cm for $\lambda2600$ $[M]^{25}_{max}=-\dfrac{49.5878}{\lambda^2-0.0365}+\dfrac{45.4628}{\lambda^2-0.029}$			Constants of sample: $d_4^{25}=1.1640$, $n_D^{25}=1.4697$ Visible region: $l=10$ cm U.V. region: $l=1$ cm $\alpha=-\dfrac{29.976}{\lambda^2-0.041}+\dfrac{26.986}{\lambda^2-0.030}$	
λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}
6678.1	-28.78	-19.87_6	5875.6	-14.636	-12.700	5780.1	-13.552
5875.6	-39.095	-27.000	5780.1	-15.286	-17.616	5460.7	-15.927
5780.1	-40.688	-28.100	5460.7	-17.875	-20.600	4358.3	-32.53
5460.7	-46.860	-32.363	4358.3	-35.305	-40.687	4046.6	-42.42
4358.3	-85.63	-59.069	4046.6	-45.39	-52.31	3910	-4.90
4046.6	-106.29	-73.406	3830	-13.9	-64.1	3810	-5.40
3840	-31.13	-86.00	3635	-16.9	-77.9	3740	-5.90
3668	-36.14	-99.84	3528	-18.9	-87.1	3665	-6.40
3525	-41.14	-113.6	3450	-20.9	-63.4	3595	-6.90
3414	-46.15	-127.5	3405	-21.9	-100.9	3490	-7.90
3320	-51.15	-141.3	3340	-23.9	-110.1	3200	-1.20 (1 mm)
3240	-56.15	-155.1	3310	-24.9	-114.8	3100	-1.40 (1 mm)
3108	-66.17	-182.8	3250	-26.9	-124.0		
2998	-76.18	-210.4	3200	-28.9	-133.2		
2915	-86.19	-238.1	3177	-29.9	-137.8		
2844	-96.20	-265.7	3135	-31.9	-147.0		
2785	-106.2	-293.4	3090	-33.9	-156.3		
2735	-116.2	-321.0	3075	-34.9	-160.9		
2690	-126.2	-348.6	3040	-36.9	-170.1		
2650	-136.2	-376.2	3010	-38.9	-179.3		
2615	-146.2	-403.9	2960	-41.9	-193.1		
2599	-151.2_5	-417.8	2920	-9.0	-207		
2440	-4.5_0	$-62._2$	2890	-9.5	-219		
2420	-4.7_5	$-65._6$	2867	-10.0	-230		
2400	-5.0_0	$-69._1$	2840	-10.5	-242		
2384	-5.2_5	$-72._5$	2775	-12.0	-276		
2340	-2.9_0	$-80._1$	2600	-1.8	-415		

asymmetric center would be analogous to the phenomena observed in the series of aldehydes.

The rotatory dispersions of the configurationally related substances given in Table I were determined. For reasons discussed in another article,[2] identical direction of rotation was assigned to configurationally related secondary carbinols and halides.

For the sake of convenience the corresponding saturated carbinols have been included in Table I.

ABSORPTION SPECTRA

It is known that the first intense absorption region of an aliphatic unsaturated hydrocarbon with only one double bond is located at about $\lambda1900-\lambda1850$.[3] Fig. 1 represents the absorption curves of two carbinols and of their corresponding chlorides. Inspection of the curves brings out two facts: First, the substitution of the chlorine atom for the hydroxyl group enhances considerably the absorption of the unsaturated compound; second, the nearer the distance between the double bond and the functional group (hydroxyl group or chlorine atom), the stronger the absorption. These results were to be expected from the knowledge of absorption spectra of organic molecules.

ROTATORY DISPERSION

The rotatory dispersion measurements are summarized in Tables II to V.

[2] P. A. Levene and A. Rothen, J. Biol. Chem. **121**, 747 (1937).

[3] C. P. Snow and C. B. Allsopp, Trans. Faraday Soc. **30**, 93 (1934).

TABLE III. *Rotatory dispersion of levo-1-octene-3-ol (vinyl-amyl carbinol) and the corresponding chloride, levo 3-chloro-octene-1, in heptane solution.*

CARBINOL
Constants of sample:
$d_4^{25} = 0.8324$ (in vacuum),
$n_D^{25} = 1.4346$
Concentration $= 1.0167\ M$
Visible region:
$l = 40$ cm
U.V. region:
$l = 10$ cm from λ3685 to λ2650, 1 cm from λ2560 to λ2350, 0.1 cm for λ2200

$$[M]^{25}_{max} = -\frac{32.496}{\lambda^2 - 0.0365} + \frac{23.669}{\lambda^2 - 0.022}$$

CHLORIDE
Concentration $= 0.777\ M$, $l = 10$ cm, 1 cm for λ2600 and λ2575, 0.1 cm for λ2370

$$[M]^{25}_{max} = -\frac{65.32}{\lambda^2 - 0.037} + \frac{60.22}{\lambda^2 - 0.010}$$

λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$
6678.1	−6.575	−23.50	4000	−1.90	−127
5875.6	−8.952	−31.994	3800	−2.40	−160
5780.1	−9.333	−33.356	3640	−2.90	−193
5460.7	−10.761	−38.460	3510	−3.40	−227
4358.3	−19.82	−70.84	3410	−3.90	−260
3685	−6.9	−118	3315	−4.40	−293
3420	−8.9	−152	3245	−4.90	−327
3170	−11.9	−204	3170	−5.40	−360
2951	−15.9	−272	3120	−5.90	−393
2850	−18.9	−323	3020	−6.90	−460
2770	−21.9	−375	2960	−7.40	−493
2650	−27.9	−477	2930	−7.90	−527
2560	−3.5	−600	2875	−8.90	−593
2540	−3.7	−630	2820	−9.90	−660
2460	−4.5	−770	2780	−10.90	−727
2438	−4.8	−820	2600	−1.50	−1000
2417	−5.1	−870	2575	−1.60	−1070
2390	−5.6	−960	2370	−0.30	−2000
2373	−5.9	−1010			
2350	−6.2	−1060			
2200	−1.1$_5$	−1970			

TABLE IV. *Rotatory dispersion of levo-1-penten-4-ol (methyl-allyl carbinol) and the corresponding chloride in homogeneous state.*

CARBINOL
Constants of sample:
$d_4^{25} = 0.8327$ (in vacuum)
$n_D^{25} = 1.4220$
Visible region:
$l = 10$ cm
U.V. region:
$l = 5$ cm, 1 cm for λ3060

$$[M]^{25}_{max} = -\frac{1.4070}{\lambda^2 - 0.046}$$

CHLORIDE
Constants of sample:
$d_4^{25} = 0.8794$ (in vacuum)
$n_D^{25} = 1.4218$
Visible region:
$l = 10$ cm
U.V. region:
$l = 5$ cm, 1 cm from λ2715 to λ2640

$$[M]^{25}_{max} = -\frac{15.474}{\lambda^2 - 0.026} + \frac{9.6138}{\lambda^2 - 0.013}$$

λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$
5875.6	−1.415	−4.700	5875.6	−5.100	−19.50
5780.1	−1.469	−4.879	5780.1	−5.305	−20.28
5460.7	−1.682	−5.587	5460.7	−6.049	−23.12
4358.3	−2.95	−9.80	4358.3	−10.47$_5$	−40.05
4046.6	−3.57	−11.86	4046.6	−12.70	−48.56
3855	−2.10	−13.9	3875	−7.10	−54.3
3715	−2.35	−15.6	3700	−8.10	−61.9
3585	−2.60	−17.3	3550	−9.10	−69.6
3475	−2.85	−18.9	3420	−10.10	−77.2
3370	−3.10	−20.6	3312	−11.10	−84.9
3300	−3.35	−22.2	3220	−12.10	−92.5
3060	−0.90	−30	3143	−13.10	−100.2
			3070	−14.10	−107.8
			3013	−15.10	−115.5
			2900	−17.10	−130.8
			2860	−18.10	−138.4
			2810	−19.10	−146.0
			2778	−20.10	−153.7
			2755	−20.60	−157.5
			2715	−4.35	−166
			2670	−4.60	−176
			2640	−4.85	−185

SUBSTANCES WITH THE ETHYLENIC GROUP ATTACHED TO THE ASYMMETRIC CARBON ATOM

From the tables it can be noticed first that the rotation of 2-penten-4-ol is opposite in sign in homogeneous state and in ether solution. Many other similar cases are known.[4] It has been pointed out in other articles that this phenomenon occurs only when the two principal partial rotations are of opposite sign. In one state the first partial rotation has a higher numerical value, whereas in the other it has a lower value than the other partial rotation. In one state the rotatory dispersion is anomalous. The rotatory dispersion of 2-penten-4-ol proved anomalous in ether solution.[5]

As seen from Tables II, III and V, *the vinyl and crotonyl derivatives (carbinols and chlorides)* are extremely dispersive and from that point of view they differ widely from the corresponding saturated substances. This great increase in the dispersive power results from the two following causes. First, the first optically active band is located nearer in the U.V. region. Second, the two principal partial rotations are of opposite sign and not much different in magnitude.

The rotatory dispersion of a few carbinols belonging to the vinyl series (methyl-, ethyl-, propyl- and butylvinylcarbinols) have already been investigated in the visible region by Kenyon and Snellgrove.[6] These authors came to

[4] P. A. Levene and A. Rothen, J. Biol. Chem. **116**, 209 (1936).

[5] We wish to correct an error which appeared in previous papers on unsaturated derivatives [J. Biol. Chem. **83**, 579 (1929); J. Org. Chem. **1**, 76 (1936)]. The fact that the rotation of 2-penten-4-ol can be of either sign, according as the measurements are taken in ether or in homogeneous state, had been overlooked and the wrong sign of rotation was attributed to this compound for comparison with other related unsaturated carbinols.

[6] J. Kenyon and D. R. Snellgrove, J. Chem. Soc. **127**, 1169 (1925).

TABLE V. *Rotatory dispersion of 2-penten-4-ol (methylcrotonyl carbinol) and the corresponding chloride.*

CARBINOL					CHLORIDE		
in Homogeneous State			in Ether Solution		in Homogeneous State		
Constants of sample: $d_4^{25}=0.8305$ (in vacuum), $n_D^{25}=1.4264$ Visible region: $l=20$ cm U.V. region: $l=5$ cm $[M]^{25}_{max}=-\dfrac{6.558}{\lambda^2-0.0365}+\dfrac{6.767}{\lambda^2-0.022}$			Concentration $=1.098\ M$, $l=40$ cm $[M]^{25}_{max}=-\dfrac{5.593}{\lambda^2-0.0365}+\dfrac{8.261}{\lambda^2-0.022}$		Constants of sample: $d_4^{25}=0.885_5$ (in vacuum), $n_D^{25}=1.4310$ Visible region: $l=10$ cm U.V. region: $l=5$ cm 1 cm from $\lambda 3080$ to $\lambda 2820$ $[M]^{25}_{max}=-\dfrac{27.03}{\lambda^2-0.0365}+\dfrac{23.57}{\lambda^2-0.029}$		
λ	α^{25}	$[M]^{25}_{max}$	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$
5875.6	−0.202	−0.303	+1.163	+7.67₅	5780.1	−1.147	−13.55
5780.1	−0.236	−0.354	+1.291	+8.52	5460.7	−1.333	−15.75
5460.7	−0.373	−0.559	+1.93	+12.7	4358.3	−2.53	−29.9
4358.3	−1.63	−2.44	+2.13	+14.3	4046.6	−3.17	−37.5
4046.6	−2.53	−3.80			3750	−2.05	−48.4
3750	−1.00	−6.00			3535	−2.55	−60.2
3600	−1.25	−7.50			3450	−2.80	−66.1
3500	−1.50	−9.00			3380	−3.05	−72.1
					3080	−0.87	−103
3400	−1.75	−10.5			3020	−0.97	−114
3320	−2.00	−12.0			2960	−1.07	−126
3275	−2.25	−13.5			2920	−1.17	−138
3230	−2.50	−15.0			2820	−1.37	−162
3170	−2.75	−16.5					
3140	−3.00	−18.0					

the conclusion that the dispersion of such compounds could be represented by a single Drude term, the λ_0^2 values increasing slightly in the series from 0.0528 for the methyl derivative to 0.0582 for the butyl derivative. Our more accurate measurements, however, show that there is a discrepancy amounting to ≃0.6 percent for the visible range between experimental values and those calculated from a single Drude term. In the U.V. region the discrepancies increase and the course of dispersion deviates strongly from that required by a single term. Analysis shows that the rotatory dispersion is fairly well expressed by two terms opposite in sign, the dispersion constant of the first term being $\lambda_1^2=0.0365$.

The fact that the same value has been found for the chlorides permits the conclusion that for the chlorides as well as for the carbinols the first major contribution is located in the double bond. These results show that the absorption region $\lambda 2400-\lambda 2000$ (which is a region of weak absorption for the vinyl carbinols but of strong absorption for the vinyl chlorides) does not

furnish an appreciable rotatory contribution contrary to the expectation based on rotatory dispersion measurements of small accuracy limited to the visible range. The dispersion constants $\lambda_0^2=0.0528$ to $\lambda_0^2=0.0582$ have no physical significance.

Attention is called to the fact that vinylamyl carbinol and crotonylmethyl carbinol have the same sign of rotation when the two corresponding saturated carbinols obtained from them by hydrogenation rotate in opposite directions. This phenomenon may be explained by the following considerations. In secondary saturated carbinols the rotation is determined by the clockwise or counterclockwise arrangement of

the groups $R_1-\overset{\displaystyle |}{\underset{\displaystyle H}{C}}-R_3$ according to their volume.

The sign of rotation is the same in all members having $R_1<R_3$; the sign is opposite in members having $R_3<R_1$. In the vinyl or crotonyl derivatives, the major partial rotation is furnished by the ethylenic group. The sign of this partial rotation is determined by clockwise or counter-

clockwise arrangement (by volume) of the groups

$$H - \overset{\displaystyle |}{\underset{\displaystyle |}{C}} - OH.$$ The arrangement does not change

with the change of R from a group of a smaller to that of a higher volume since when $R = CH_3$, the volume of the methyl group is already larger than that of the remaining two groups.

EFFECT OF THE INCREASE IN DISTANCE OF THE ETHYLENIC GROUP FROM THE ASYMMETRIC CENTER

In this connection 1-penten-4-ol will be discussed. The rotatory measurements are summarized in Table IV. It may be seen that in this case carbinol and halide are considerably less dispersive than the corresponding vinyl or crotonyl derivatives. The small rotation of the alkyl carbinol did not permit the resolution of the dispersion curve into two terms, but the analysis of the dispersion of the chloride shows that the origin of the first rotatory contribution is located further in the ultraviolet region ($\lambda_1^2 = 0.026$) than the first partial rotation of the vinyl derivatives. In fact the value of the dispersion constant of the first contribution of this substance is nearly the same as that of the *second* partial contribution of the vinyl or crotonyl series. Hence for the chlorides it might be assumed that corresponding bands in members of the two series—alkyl and vinyl or crotonyl series—are of opposite sign. On the other hand, the absorption region corresponding to $\lambda_1^2 = 0.036$ furnishes an insignificant contribution in methylalkyl carbinol. Thus the effect of the distance from the asymmetric center of the significant chromophoric group is not brought out clearly in the case of ethylenic derivatives. Nevertheless the value of the first dispersion constant of alkylmethyl carbinol seems to indicate that the effect of distance exists also in the ethylenic series. It is not impossible that in the higher homologues of the alkyl series the effect of distance will come more clearly to the front.

EXPERIMENTAL

Compounds

The compounds were carefully fractionated and titration of the double bond by bromine was carried out for each of them.

The maximum molecular rotations have been calculated from the accepted maximum values for the saturated carbinols and from the values of the rotations of the saturated carbinols obtained by reduction of the unsaturated ones. The degree of racemization occurring in the preparation of the chlorides from the carbinols being unknown, the maximum values given for the former are only minimum values. They are "least maximum values."

The rotatory measurements were carried out as previously described. The same precautions were taken and the same precision is claimed.

The agreement between observed and calculated values from a two term formula is satisfactory.

For vinylbutyl carbinol, the deviations between experimental and calculated rotations are within experimental error over the visible range of the spectrum (<0.05 percent). In the U.V. range, deviations >0.5 percent do not occur.

For vinylamyl carbinol, the deviations are greater, 0.1 percent in the visible range and from 1 to 5 percent in the U.V. range. The deviations are systematic and would probably be reduced by splitting the second term into two terms of opposite sign. The small angles of rotation observed did not seem to warrant this calculation.

For 3-chloroheptene-1 the deviations observed are 0.05 percent in the visible range and 0.5 percent in the U.V. region. Discrepancies of the order of 1 percent are observed for 3-chlorooctene-1, no rotation being measured in the visible range of the spectrum.