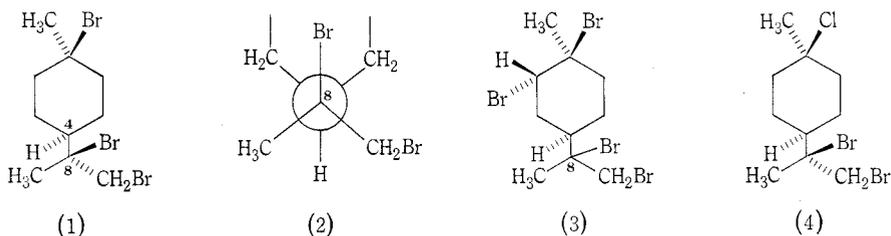


## THE OPTICAL ROTATION OF VICINAL DIBROMIDES

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The optical rotation of dibromides at the  $\text{Na}_D$  line is covered by Brewster's Rules.<sup>1-5</sup> However, without modification, Brewster's Rules can give anomalous results for 1,2-dibromides. For instance, diaxial (1*R*,2*R*)-1,2-dibromocyclohexane is predicted to have a zero rotation whereas its value is appreciably negative.<sup>6</sup> The rotation of the (8*S*)-tribromo-*p*-menthane derivative (1), in which the rotation is presumably due to conformer (2) about the C4-C8 bond, is predicted by Brewster's Rules to be zero when the  $\text{CH}_2\text{Br}$  group is treated as  $\text{CH}_3$ ; or to be negative if  $\text{CH}_2\text{Br}$  is more polarizable than  $\text{CH}_3$ . In fact,<sup>7</sup> compound (1) has a positive rotation. Similarly, the 8*R* and 8*S* isomers of limonene tetrabromide (3) differ in rotation<sup>7</sup> in a manner unexpected from a simple application of Brewster's Rules.



These anomalies are removed when it is realized that the CBr-CBr bond is *less* polarizable than a C-C bond. Similarly, the carbon-bromine bond is less polarizable in CBr-C-Br than in C-C-Br. There is, of course, chemical evidence which supports the above assertions.

The group CBr when attached to a carbon also carrying bromine is designated CBr\*. From averaged values for compounds (1) and (3):

$$k(\text{C-H})(\text{CBr}^*\text{-H}) \simeq 10$$

i.e. the polarizability of CBr\* is empirically only slightly greater than that of H.

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<sup>1</sup> Brewster, J. H., *J. Am. chem. Soc.*, 1959, **81**, 5475.

<sup>2</sup> Brewster, J. H., *J. Am. chem. Soc.*, 1959, **81**, 5483.

<sup>3</sup> Brewster, J. H., *Tetrahedron*, 1961, **13**, 106.

<sup>4</sup> Eliel, E. L., "Stereochemistry of Carbon Compounds." p. 403. (McGraw-Hill: New York 1962.)

<sup>5</sup> Brewster, J. H., in "Topics in Stereochemistry." Vol. 2, p. 24. (Eds N. L. Allinger and E. L. Eliel.) (Interscience: New York 1967.)

<sup>6</sup> Applequist, D. E., and Weiner, N. D., *J. org. Chem.*, 1963, **28**, 48.

<sup>7</sup> Carman, R. M., and Venzke, B. N., *Aust. J. Chem.*, 1971, **24**, 1727.

TABLE I  
COMPARISON OF PREDICTED AND FOUND  $[M]_D$  VALUES

$\Delta[M]_D$ , difference between the molecular rotation of the bromide and the corresponding hydrocarbon; "predicted"  $\Delta[M]_D$  from values given in the Discussion, "calculated"  $\Delta[M]_D$  from Brewster's values<sup>a</sup>

Compound	$\Delta[M]_D$	$\Delta[M]_D$	$\Delta[M]_D$
	Predicted	Found	Calc.
Compound (1) <sup>7</sup>	+50	+66	0
Compound (3) (8 <i>S</i> isomer) <sup>7</sup>	+320	+338	+180
Compound (3) (8 <i>R</i> isomer) <sup>7</sup>	+220	+296	+180
Compound (4) <sup>7</sup>	+50	+16	0
Sylvestrene tetrabromide <sup>8</sup>	+270 ± 50 <sup>a</sup>	+336	+180
1 $\alpha$ ,2 $\beta$ -Dibromocholestane <sup>6</sup>	+90	+117	+180
2 $\beta$ ,3 $\alpha$ -Dibromocholestane <sup>9</sup>	+110 <sup>b</sup>	+314	0
2 $\alpha$ ,3 $\beta$ -Dibromocholestane <sup>9</sup>	-290	-243	-610
3 $\beta$ ,4 $\alpha$ -Dibromocholestane <sup>9</sup>	+140	+102	+430
3 $\alpha$ ,4 $\beta$ -Dibromocholestane <sup>9</sup>	+40 <sup>c</sup>	-62	+180
5 $\beta$ ,6 $\alpha$ -Dibromocholestane <sup>10</sup>	+330	+182	+610
5 $\alpha$ ,6 $\beta$ -Dibromocholestane <sup>10</sup>	-280	-296	-180
2 $\beta$ ,3 $\alpha$ -Dibromo-3 $\beta$ -methylcholestane <sup>11</sup>	+260 <sup>d</sup>	+396	+180
2 $\alpha$ ,3 $\beta$ -Dibromo-3 $\alpha$ -methylcholestane <sup>11</sup>	-140	-170	-430
(1 <i>R</i> ,3 <i>S</i> ,4 <i>S</i> )-3,4-Dibromomethylcyclohexane <sup>12</sup>	+120 <sup>e</sup>	+218 <sup>f</sup>	0
(1 <i>R</i> ,3 <i>R</i> ,4 <i>R</i> )-3,4-Dibromomethylcyclohexane <sup>12</sup>	-280 <sup>g</sup>	-423 <sup>f</sup>	-610
(1 <i>R</i> ,2 <i>R</i> )-Dibromocyclohexane (diaxial) <sup>6,13</sup>	-120	-28(?) <sup>f</sup>	0
(1 <i>R</i> ,2 <i>R</i> )-Dibromocyclohexane (diequatorial) <sup>6,13</sup>	-280	-100(?) <sup>f</sup>	-610
(1 <i>S</i> ,2 <i>S</i> ,3 <i>S</i> )-2,3-Dibromomethylcyclohexane <sup>14</sup>	-30 <sup>h</sup>	+87 <sup>i</sup>	-180
(1 <i>S</i> ,2 <i>R</i> ,3 <i>R</i> )-2,3-Dibromomethylcyclohexane <sup>14</sup>	-130 <sup>j</sup>	-514 <sup>i</sup>	-430
(1 <i>R</i> ,3 <i>S</i> ,4 <i>S</i> )-3,4-Dibromo- <i>t</i> -butylcyclohexane <sup>14</sup>	+120 <sup>k</sup>	+247 <sup>i</sup>	0
(1 <i>R</i> ,3 <i>R</i> ,4 <i>R</i> )-3,4-Dibromo- <i>t</i> -butylcyclohexane <sup>14</sup>	-280 <sup>j</sup>	-391 <sup>i</sup>	-610
( <i>S</i> )-1,2-Dibromobutane <sup>15</sup>	-230 <sup>l</sup>	-51 <sup>m</sup>	-300

<sup>a</sup> Depending upon whether the C8 configuration is *R* or *S*. From these data it would appear to be *S*, and so (+)-sylvestrene tetrabromide is (1*S*,3*R*,6*S*,8*S*)-1,6,8,9-tetrabromo-*m*-menthane. <sup>b</sup> Value for diaxial dibromide. This conformation suffers a severe 1,3-diaxial Me, Br interaction. The boat form (C2, C5 bow) which eliminates this interaction has a predicted  $\Delta[M]_D$  of approx. +700. <sup>c</sup> Value for diaxial conformation which suffers a 1,3-diaxial Me, Br interaction. Predicted  $\Delta[M]_D$  for boat (C10, C3 bow) is approx. -400. <sup>d</sup> Value for diaxial dibromide. Distortion toward a boat (C2, C5 bow) form causes the rotation to become more positive. <sup>e</sup> Diaxial dibromide conformation. The diequatorial dibromide conformer is predicted to have  $[M]_D$  +290. <sup>f</sup> Values calculated in the literature to be "best" values. <sup>g</sup> The all-equatorial conformer. The all-axial conformer is predicted to have  $[M]_D$  -110. <sup>h</sup> Value for diaxial conformer. The diequatorial conformer is predicted to have  $[M]_D$  +480. <sup>i</sup> Calculated maximum value. <sup>j</sup> The triequatorial conformer. <sup>k</sup> The diaxial dibromide. <sup>l</sup> Weighing equally the two most favourable conformers about the C2-C3 bond, and considering only the antiperiplanar conformation about C1-C2. <sup>m</sup> A minimum value.

<sup>8</sup> Mathew, C. P., and Verghese, J., *Indian J. Chem.*, 1963, **1**, 229.

<sup>9</sup> Alt, G. H., and Barton, D. H. R., *J. chem. Soc.*, 1954, 4284.

<sup>10</sup> Barton, D. H. R., and Miller, E., *J. Am. chem. Soc.*, 1950, **72**, 1066.

<sup>11</sup> Barton, D. H. R., Campos-Neves, A. da S., and Cookson, R. C., *J. chem. Soc.*, 1956, 3500.

<sup>12</sup> Bellucci, G., Giordano, C., Marsili, A., and Berti, G., *Tetrahedron*, 1969, **25**, 4515.

<sup>13</sup> Berti, G., and Marsili, A., *Tetrahedron*, 1966, **22**, 2977.

<sup>14</sup> Bellucci, G., Berti, G., Marioni, F., and Marsili, A., *Tetrahedron*, 1970, **26**, 4627.

<sup>15</sup> Bellucci, G., Marioni, F., and Marsili, A., *Tetrahedron*, 1969, **25**, 4167.

The group Br when bonded in the system CBr-CBr is designated Br\*. Empirically we assign a value of +400 to the expression  $k(\text{Br}^*-\text{H})^2$ , and a value of +70 to the expression  $k(\text{C}-\text{H})(\text{CBr}-\text{H})$  where CBr is the C-CBr system with no bromine on the first carbon atom. This bond is predicted to be slightly more polarizable than the C-C bond. The above assignments lead to apparent refractivities of 1.24, 3.05, and 6.65 for the groups CBr\*, CBr, and Br\* respectively, and they give the expression:

$$k(\text{C}-\text{H})(\text{Br}^*-\text{H}) = +150$$

Comparisons between literature values for the molecular rotation of vicinal dibromides, and values calculated from the above expression, are listed in Table 1. Also included are values calculated from Brewster's original values. In general, the present agreement is good although lack of knowledge of the geometry of the exact conformation, or of the conformational distribution, may lead to some discrepancies.

It is obvious that the values listed above for CBr\*, CBr, and Br\* may require refinement as more compounds and conformational data become available, but the concept that the bond CBr-CBr has a vastly smaller polarizability than the C-C bond appears to be valid and useful in predicting molecular rotations.