

tended one by stretching in which the fiber period lengthens (as from 20.5 to 26.5 Å.) and the structure changes also. This behavior is reminiscent of fibrous proteins, as are many other properties of these polymers.

Similar retraction phenomena have been introduced in normally extended, unsubstituted polyamides by allowing plasticizers, such as cresol, to penetrate into the polar layers. The resulting structural changes demonstrate polar association

of the plasticizer, often considered as a mechanism for plasticizer action.

A possible explanation of chain twisting is that it results from a compromise of the packing tendencies of the paraffin sections and polar sections of the chain. In general, it may reflect competing packing tendencies.

The chain retraction and extension observed may be the first stages of rubbery elasticity.

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Raman Spectra of Four Pairs of *meso* and *dl* Disubstituted Butanes

BY HARVEY J. TAUFEN, M. J. MURRAY AND FORREST F. CLEVELAND

Weissberger¹ has pointed out that since *meso* and *dl* compounds possess different dipole moments, they do not have free rotation about the carbon-carbon single bond. The use of these differences for assignment of structure has been shown by Winstein and Wood² to be of no general application. However, of the diastereomers examined^{1,2} which possess no angular polar groups, the *dl* isomer has the larger dipole moment with the exception of the 2,3-dibromobutanes. Electron diffraction measurements³ of this pair have shown that in the equilibrium position both these compounds have the bromine atoms *trans* to each other. It has been pointed out^{2,3} that this would lead to a small dipole moment and that the observed moment must, therefore, arise not only from the equilibrium configuration but also from the vibrations and rotations (librations) about

the carbon-carbon bond. This also suggests the presence of rotational isomers (in amounts undetectable by electron diffraction), whose presence could aid in correlating the dipole moment data (see Fig. 1). The detection of rotational isomers by the Raman effect has been the subject of lengthy investigations by Kohlrausch and co-workers,⁴ Glockler and co-workers,⁵ Mizushima and Morino,⁶ and others with quite satisfactory results in many cases.

In the present investigation the Raman spectra of *meso*- and *dl*-2,3-dibromobutane, *meso*- and *dl*-2,3-dichlorobutane, *meso*- and *dl*-2,3-diacetoxybutane, and *meso*- and *dl*-2,3-butanediol have been obtained and studied. Kohlrausch and his co-workers⁷ have previously examined 2,3-dibromobutane and 2,3-dichlorobutane and reported in the former case that only the *trans* configuration was present. A mixture of isomers was employed in both these investigations, however, and weaker lines due to one or the other structural isomer could therefore have been easily overlooked.

Trieschmann⁸ has obtained the Raman spectra of *dl*- and *meso*-2,3-dibromobutane, but the compounds which he used were of doubtful purity² and the data which he reported were incomplete.

Diastereomeric pairs often show no large differences in physical properties, which makes de-

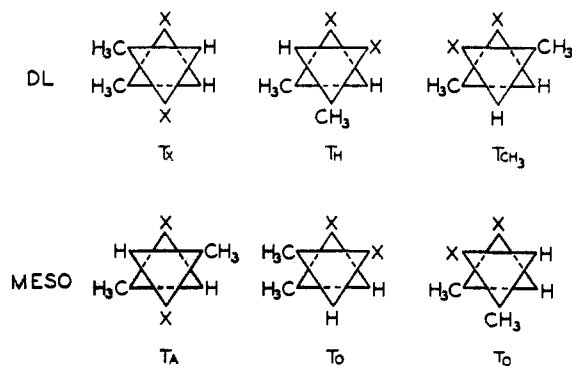


Fig. 1.—Possible rotational isomers for diastereomeric 2,3-disubstituted butanes.

- (1) Weissberger, *J. Org. Chem.*, **2**, 245 (1937).
- (2) Winstein and Wood, *THIS JOURNAL*, **62**, 548 (1940).
- (3) Stevenson and Schomaker, *ibid.*, **61**, 3173 (1939).

(4) Kohlrausch, "Der Smekal-Raman-Effekt, Ergänzungsband," Julius Springer, Berlin, 1938, p. 169.

(5) Edgell and Glockler, *J. Chem. Phys.*, **9**, 375 (1941).

(6) Mizushima and Morino, "Raman Jubilee Volume," 1938, p. 315.

(7) Kohlrausch and Ypsilanti, *Z. physik. Chem.*, **B32**, 407 (1936); Kahovec and Kohlrausch, *ibid.*, **B45**, 7 (1940).

(8) Trieschmann, *ibid.*, **B32**, 283 (1936).

TABLE I
RAMAN SPECTRA OF DIASTEREOMERS, DICHLORO- AND DIBROMOBUTANES

| 2,3-Dichlorobutane | | | | | | 2,3-Dibromobutane | | | | | |
|--------------------|-----------------------|--------|-------------|-------------------------|--------|-------------------|-----------------------|--------|-------------|-------------------------|--------|
| $\Delta\nu$ | <i>dl</i> <i>I</i> | ρ | $\Delta\nu$ | <i>meso</i> <i>I</i> | ρ | $\Delta\nu$ | <i>dl</i> <i>I</i> | ρ | $\Delta\nu$ | <i>meso</i> <i>I</i> | ρ |
| 108 | 10 | | 100 | 5 | | 154 | 2 | | 146 | 1 | |
| 199 | 1 | | 192 | 1 | | 182 | 45 | 0.25 | 186 | 40 | 0.2 |
| 229 | w | | 267 | w | | 202 | 1 | | 234 | 2 | .6 |
| 267 | 4 | 0.5 | 282 | 5 | 0.6 | 274 | 5 | .3 | 298 | 8 | .3 |
| 309 | 1 | P | 306 | w | | 307 | 20 | .2 | | | |
| 346 | 2 | | 347 | 7 | .6 | 360 | 1 | P | 361 | 8 | .15 |
| 373 | 12 | .4 | | | | 447 | 1 | .7 | | | |
| 434 | 2 | | 422 | 8 | .25 | | | | 468 | 16 | .2 |
| 487 | 2 | | 486 | 6 | .15 | 502 | 15 | .1 | | | |
| 524 | 3 | D | 535 | 3 | .4 | 540 | 2 | .8 | | | |
| 599 | 12 | .3 | | | | 563 | w | | 600 | 9 | .15 |
| 653 | 1 | | 652 | 15 | .15 | 633 | 100 | .2 | 632 | 100 | .25 |
| 695 | 45 | .35 | 703 | 50 | .4 | | | | | | |
| 831 | 5 | .75 | | | | 825 | 20 | .5 | | | |
| 855 | 2 | D | 848 | 6 | .8 | 846 | 2 | P | 840 | 20 | .5 |
| 956 | 1 | | | | | 949 | 1 | D | 962 | 1 | .8 |
| 978 | w | | 970 | 2 | D | | | | | | |
| 999 | 1 | | 1020 | 2 | D | 1003 | 3 | .4 | 999 | 2 | .6 |
| 1023 | 3 | P | 1056 | 1 | | 1038 | 1 | | 1035 | 1 | |
| | | | 1092 | 1 | | | | | 1070 | 1 | .7 |
| 1129 | 2 | P | 1124 | 1 | | 1102 | 1 | | 1117 | 1 | D |
| 1168 | 2 | P | 1162 | 2 | | 1158 | 3 | .4 | 1150 | 18 | .4 |
| | | | | | | 1188 | 3 | P | 1197 | 2 | P |
| 1231 | 3 | | 1235 | w | | 1211 | 20 | .35 | 1215 | 16 | .35 |
| 1257 | 4 | P | 1253 | 6 | .8 | | | | | | |
| 1308 | 1 | | 1332 | 1/2 | | | | | 1358 | 1 | .7 |
| 1382 | w | | 1360 | 1/2 | P | 1380 | 1 | | 1382 | 1 | .7 |
| | | | 1386 | 1/2 | P | 1444 | 5 | .75 | 1447 | 6 | .7 |
| 1451 | 8 | .8 | 1453 | 8 | .8 | 1458 | 1 | | | | |
| 2741 | 2 | | 2742 | 2 | | 2741 | w | | 2740 | 1 | |
| 2870 | 7 | .15 | 2872 | 7 | .2 | 2867 | 2 | P | 2866 | 4 | .4 |
| 2937 | 100 | .2 | 2938 | 100 | .15 | 2930 | 25 | .15 | 2930 | 60 | .1 |
| 2974 | } 30 | .55 | 2991 | 35 | .4 | 2976 | 20 | .6 | 2978 | } 23 | .6 |
| 2990 | | | | | | 9 | | 2994 | | | |

termination of purity a difficult task. Differences in the Raman spectra⁹ should aid in determining whether isomerization occurs in the syntheses that have been developed for diastereomeric compounds.

Experimental

meso-2,3-Butanediol was Lucidol Corporation material and was separated from the *dl* compound by four recrystallizations from diethyl ether; m. p. 34.2–34.4°, b. p. 180.8–181.0°.

dl-2,3-Butanediol was prepared by saponification of *dl*-2,3-diacetoxybutane (sample, m. p. 42.9°) according to a method suggested by Dr. Saul Winstein. Normal sodium hydroxide was prepared by dissolving sodium in absolute alcohol and adding an equivalent amount of water. The diacetoxybutane in a minimum amount of absolute alcohol was added dropwise to this hot solution. The alcohol was then stripped off to one-fourth the original volume and enough dry ether added to precipitate the sodium acetate.

(9) Differences in the Raman spectra of *meso*- and *d*-tartaric acid in hydrochloric acid solution have been observed previously by Edsall, *J. Chem. Phys.*, **5**, 508 (1937).

After filtration the butanediol was obtained by distillation; b. p. 89° at 19.5 mm.

meso-2,3-Diacetoxybutane was prepared from *meso*-2,3-butanediol by the method of Wilson and Lucas,¹⁰ b. p. 73° at 8 mm.; yield 83%.

dl-2,3-Diacetoxybutane was prepared from *dl*-2,3-dibromobutane by the method of Winstein and Buckles¹¹; yield 75%; m. p. 39.6°. Recrystallization from low-boiling petroleum ether raised the melting point to 43.0°.

meso-2,3-Dibromobutane was prepared from *dl*-2,3-diacetoxybutane by the method of Wilson and Lucas¹⁰; b. p. 73–74° at 50 mm., yield 93%.

dl-2,3-Dibromobutane was prepared analogously from *meso*-2,3-diacetoxybutane; b. p. 76° at 50 mm.; yield 95%.

dl-2,3-Dichlorobutane was prepared from *cis*-2-butene by the method of Lucas and Gould.¹² The apparatus was modified, in that the gases were introduced at the bottom of the reaction chamber; b. p. 53.0–53.5° at 81 mm. The *cis*-2-butene was prepared¹² from *dl*-2,3-dibromobutane.

(10) Wilson and Lucas, *THIS JOURNAL*, **58**, 2396 (1936).

(11) Winstein and Buckles, *ibid.*, **64**, 2780 (1942).

(12) Lucas and Gould, *ibid.*, **68**, 2541 (1941).

meso-2,3-Dichlorobutane was prepared from *meso*-2,3-dibromobutane in one apparatus. The *trans*-2-butene was generated analogously to the *cis*-2-butene and passed into the chlorination apparatus after the usual washing and drying; b. p. 49.0–50.5° at 80 mm.; yield 60%, based on *meso*-2,3-dibromobutane.

All the distillations were carried out using a 30-cm. Podbielniak-type column with controlled reflux ratio.

The spectrograph and method of obtaining the Raman frequencies have been described earlier.¹³ The members of each pair of diastereomers were given the same exposure to allow a qualitative comparison of intensity. A Gaertner microdensitometer was used to determine the intensities and the depolarization factors. The instrument was calibrated by varying the distance of a tungsten lamp from a piece of white cardboard, placed at the position of the Raman tube, so as to obtain illuminations of known relative intensities. The intensity of the background was subtracted from that of the line in each case. All the diastereomers were examined in the liquid state, a heating element on the tube being employed to keep *dl*-2,3-diacetoxybutane in the molten condition.

Discussion

The Raman spectra for the diastereomers are listed in Tables I and II. The intensity of the strongest line in each spectrum is arbitrarily given the value of 100. Lines too weak for densitometer readings are listed as w. The results are shown graphically in Fig. 2, in which the height of the line represents a visual estimate of intensity.

For every diastereomeric pair, distinct differences well above the experimental error are observed in the Raman spectra. This is especially true in the chlorobutanes and the bromobutanes, an effect to be anticipated, since in these compounds the strongest lines arise from vibrations involving valence bonds directly affected by the stereoisomerism.

Molecules as complicated as the substituted butanes do not yield readily to a rigorous analysis, and for this reason the spectra must be discussed qualitatively. It appears well established,^{4,14} however, that frequencies involving the carbon-bromine stretching vibration are in general observed in the neighborhood of 530–630 cm.⁻¹, while frequencies involving the carbon-chlorine stretching vibration fall around 600–700 cm.⁻¹. Kohlrausch and his co-workers⁴ have shown that for a large number of monohalogenated paraffins a multiplicity of lines in these regions occurs only when the structural configuration permits the presence of non-identical rotational isomers.

(13) Cleveland, Murray, Coley and Komarewsky, *J. Chem. Phys.*, **10**, 18 (1942).

(14) Branch and Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 153.

TABLE II
RAMAN SPECTRA OF DIASTEREOMERIC BUTANEDIOLS AND
DIACETOXYBUTANES

| 2,3-Butanediol | | | | 2,3-Diacetoxybutane | | | |
|----------------|----------|-------------|----------|---------------------|----------|--------------------------|----------|
| $\Delta\nu$ | <i>I</i> | $\Delta\nu$ | <i>I</i> | $\Delta\nu$ | <i>I</i> | $\Delta\nu$ | <i>I</i> |
| <i>dl</i> | | <i>meso</i> | | <i>dl</i> | | <i>meso</i> ^a | |
| 362 | w | 354 | w | 236 | 4 | 241 | w |
| | | 386 | w | 295 | w | 279 | w |
| 434 | w | 442 | w | | | 317 | w |
| 499 | w | 476 | w | 394 | 4 | 391 | 4 |
| 521 | w | 525 | 7 | | | 415 | w |
| 546 | 14 | 552 | 7 | 527 | 2 | 522 | 3 |
| | | 640 | w | | | 532 | w |
| 759 | 9 | 779 | 28 | 623 | 7 | 627 | 5 |
| 780 | w | | | 649 | 4 | 650 | 2 |
| 792 | w | | | 808 | 4 | 814 | 2 |
| 812 | 19 | 818 | 13 | 846 | 3 | 858 | w |
| 884 | 5 | 888 | 10 | 874 | 12 | 873 | 5 |
| 928 | 13 | 935 | 20 | 955 | 3 | 957 | 2 |
| 961 | 3 | | | | | 994 | 1 |
| 992 | 3 | 996 | 13 | | | 1024 | 1 |
| 1011 | w | 1008 | 1 | 1090 | w | 1088 | 1/2 |
| 1113 | 13 | 1120 | 10vb | | | 1108 | 1 |
| 1160 | 3 | 1164 | 7 | | | 1143 | 1/2 |
| | | 1318 | w | | | 1175 | 1 |
| 1367 | w | 1377 | w | 1311 | w | 1311 | 1 |
| 1399 | w | | | 1339 | 7 | 1333 | w |
| 1450 | 13 | 1458 | 24 | | | 1358 | w |
| 2721 | w | 2723 | w | | | 1376 | w |
| 2868 | 85 | 2873 | 60 | | | 1430 | w |
| | | 2905 | 1 | 1457 | 9 | 1457 | 5 |
| 2928 | 100 | 2935 | 100 | 1740 | 13 | 1742 | 5 |
| 2979 | 85 | 2987 | 80 | | | 2847 | w |
| | | | | 2879 | 10 | 2881 | 4 |
| | | | | 2942 | 100 | 2942 | 100 |
| | | | | 2994 | 20 | 2992 | 21 |

^a Spectrum obtained by Dwight C. Lincoln.

Furthermore, the multiplicity in nearly every case is equal to the number of possible rotational isomers, if only "staggered" configurations are assumed. Apparently a complete correlation of data for dihalogenated paraffins cannot be made on this basis. For example, ethylene dibromide and ethylene dichloride, which can have only two distinct isomers, have three lines each in these regions.⁶ However, it is conceivable that in some cases the multiplicity of lines is due, at least in part, to the presence of distinct rotational configurations.

Utilizing "staggered" configurations, Weissberger¹ has pointed out that there exist three rotational possibilities for a *dl* compound and only two for a *meso* compound (see Fig. 1). It is of interest to note that in the dibromobutanes the *dl*-form possesses three Raman lines in the proper region (displacements of 633, 563, and 540 cm.⁻¹), while the *meso* form shows only two (at 632 and 600 cm.⁻¹). The same effect is to be noted in the

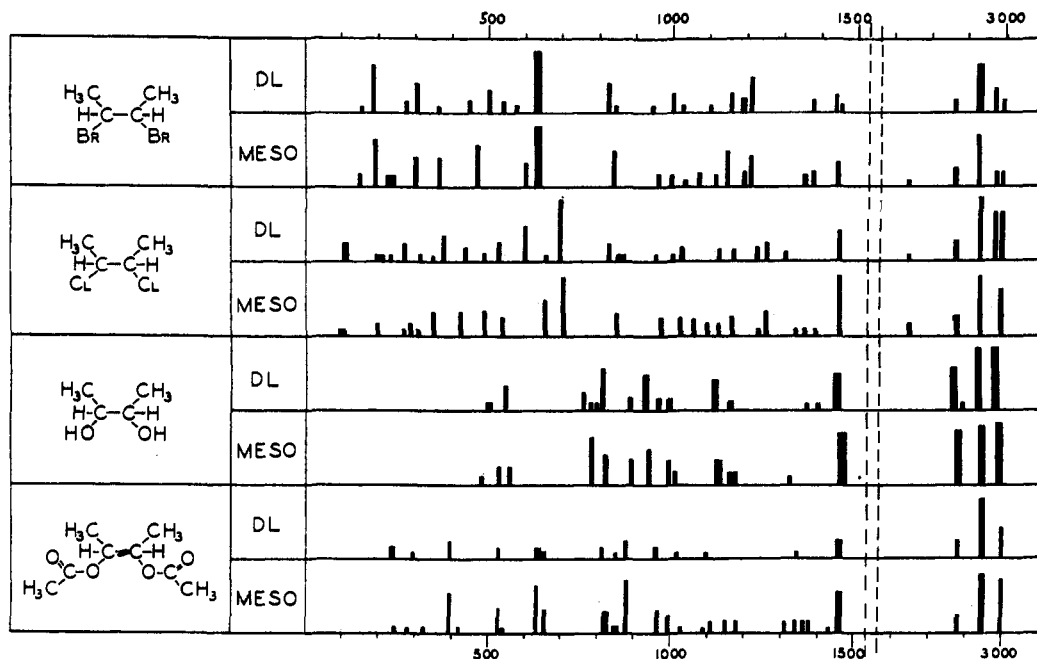


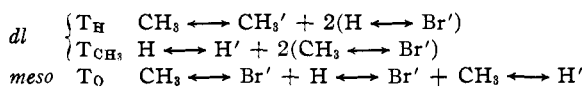
Fig. 2.—Graphical representation of the Raman spectra of four pairs of diastereomers.

chlorobutanes, the *dl* having three lines (695, 653 and 599 cm^{-1}) and the *meso* only two (703 and 652 cm^{-1}).

Stevenson and Schomaker⁸ have shown by electron diffraction that the *trans* configuration for the bromine atoms predominates in both *dl*- and *meso*-2,3-dibromobutane, although they assumed some oscillation about this position. The very intense Raman line at approximately 630 cm^{-1} in these compounds probably involves the carbon-bromine stretching vibration for this configuration. The two weak lines in the *dl* compound can be assigned to T_{CH_3} and T_{H} , and the somewhat stronger 600 cm^{-1} frequency in the *meso* compound to T_{O} (see Fig. 1). An analogous assignment of frequencies is possible for the chlorobutanes. Taking line intensity as a measure of concentration indicates that the *meso*-2,3-dibromobutane would have close to 9% of the T_{O} form, while the forms T_{CH_3} and T_{H} for the *dl* modification would total approximately 2%. These conclusions are not in disagreement with the electron diffraction data.

As a first approximation, the potential barrier to rotation can be assumed to involve chiefly the steric interactions between groups on the adjacent central carbon atoms. From the size of the groups the interactions should be $\text{CH}_3 \leftrightarrow \text{CH}_3' > \text{CH}_3 \leftrightarrow \text{X}' > \text{CH}_3 \leftrightarrow \text{H}'$, $\text{H} \leftrightarrow \text{X}'$, $\text{H} \leftrightarrow \text{H}'$ ($\text{X} = \text{Br}, \text{Cl}$). For $\text{X} \leftrightarrow \text{X}'$ the barrier due to polarity will

be high at room temperature.¹⁵ In the 2,3-dibromobutanes the following interactions occur when the molecule rotates 120° from the *trans* position



Hence, the barrier to the T_{O} form for the *meso* appears to be lower than that for either rotational isomer in the *dl*. The T_{O} form can thus account for the presence of the relatively strong line at 600 cm^{-1} in the *meso* compound and also partially explain why the *meso* compound has the larger dipole moment. Substitution of ethyl for methyl groups in the above scheme would substantially prevent the presence of all rotational isomers, and the dipole moments would then be chiefly due to oscillation about the *trans* position. The *dl* form would then be expected to have the larger moment, as is the case.²

Substitution of chlorine for bromine should lower the group interactions $\text{CH}_3 \leftrightarrow \text{X}'$. Hence, in the chlorobutanes both the T_{O} for the *meso* and the T_{CH_3} for the *dl* should be present in easily detectable amounts. Both the *meso*- (at 652 cm^{-1}) and *dl*-2,3-dichlorobutane (at 599 cm^{-1}) have a strong companion to the more intense line at approximately 700 cm^{-1} . The *dl* also has another weak line (at 653 cm^{-1}) perhaps due to T_{H} .

(15) Smyth, Dornte and Wilson, *THIS JOURNAL*, **52**, 4242 (1931).

In the foregoing considerations, coulomb forces have been considered significant only for the halogen atoms, while dispersion forces and the possibility of Fermi resonance have been neglected. Although the first two assumptions are probably valid as a first approximation, Fermi resonance is an unknown factor. Nevertheless, rotational isomerism correlates the data so well for the two pairs of diastereomers that it can hardly be ignored, at least as a possibility.

The data formerly obtained⁷ for 2,3-dibromobutane and 2,3-dichlorobutane agree well with expectations for mixtures of isomers. However, Kohlrausch and Ypsilanti⁷ fail to report the 600 cm.^{-1} frequency in the *meso* compound. Although this line would be weaker in a mixture of isomers, in view of other lines they reported it should have been detected readily. During the present work this line was easily observed also in the spectrum of a vacuum-distilled sample of Eastman Kodak Co. β -butylene bromide, which is composed of a mixture of the diastereomers.

In the case of the dibromobutanes it is believed that the sample of each diastereomer, as prepared, contains less than 2% of the other form. The basis for this conclusion rests on the absence of the strong 502 cm.^{-1} line of the *dl* from the spectrum of the *meso* and the absence of the strong 468 cm.^{-1} line of the *meso* from the spectrum of the *dl*.

With the dichlorobutanes the absence of the strong 373 and 599 cm.^{-1} lines of the *dl* from the spectrum of the *meso* indicates that any contamination of the sample of *meso* by the *dl* form must be very slight. On the other hand, it is not possible to draw conclusions about the absence or presence of significant quantities of the *meso* in the sample of *dl*. The *meso* line at 652 cm.^{-1} is the only one which has strength enough to be of real use in this matter, and it happens that the *dl* sample shows a weak line at this same position. This weak line could be a *bona fide* frequency of the *dl* or it could

be caused by the presence of approximately 6% of the *meso* form.

The butanediols and diacetoxybutanes have no strong frequencies assignable to bonds directly involved in the stereoisomerism and it is difficult to draw any conclusions from their spectra. There are, however, distinct differences in each case.

Acknowledgments.—The authors wish to thank Dr. Saul Winstein for making available the *dl*-2,3-diacetoxybutane employed in preparing the *dl*-2,3-butanediol. The microdensitometer used in obtaining the intensities was secured with a grant to one of us (F. F. C.) from the Penrose Fund of the American Philosophical Society. The optical parts in the spectrograph were secured with a grant to two of us (M. J. M. and F. F. C.) by Sigma Xi.

Summary

1. Raman spectra have been obtained for four pairs of diastereomers: *viz.*, *meso*- and *dl*-2,3-butanediol, *meso*- and *dl*-2,3-diacetoxybutane, *meso*- and *dl*-2,3-dibromobutane, and *meso*- and *dl*-2,3-dichlorobutane.

2. For each diastereomeric pair, distinct differences in spectra far above the experimental error have been observed.

3. In the case of the dibromobutanes the spectra obtained indicate that the sample of each diastereomer, as prepared, contains less than 2% of the other form. With the dichlorobutanes any contamination of the sample of *meso* by *dl* must be very small; but it is not possible to draw conclusions as to the purity of the sample of *dl* compound.

4. Multiplicities of lines in the appropriate regions have indicated the presence of rotational isomers in the halogenated butanes, and a correlation of the rotational possibilities with the spectra and with previous dipole moment data has been pointed out.

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