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Refractivity and Molecular Structure. III. Isomeric Propyl and Butyl Mercaptans

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Introduction

Since the time when the foundations of the field of refractivity were established, a considerable development in our knowledge concerning the structure of molecules has taken place. From the classical point of view, the molar refractivity, as defined by the Lorentz-Lorenz equation, has been considered as an additive and constitutive property, practically independent of the state of aggregation. It has been widely used in problems of molecular structure, usually by comparing the experimental results with values calculated from atomic, or bond and octet increments. It is the object of our investigations to contribute to a new approach toward the problem of refractivity, especially of organic compounds, in the light of modern theories of molecular structure.

The limitations of the concept of additivity were clearly presented by Fajans¹ and the evidence recently pointed out by Fajans and Cook² of an alternating polarity in alkyl chains attached to appropriate polar groups allows us to understand the nature and limitations of this concept much better than before. The atomic or bond³ and octet increments have been derived on the assumption that the refractivity is an additive property. The calculation of the increments by any one of these systems of interpretation, involves the basic assumption that the refractivity of a particular atom, bond or octet in a molecule is not influenced by the presence of the other atoms, bonds or octets. The refractivity is, however, a measure of the deformability of electronic systems. Deviations from additivity have been used as an indication and measure of tightening and loosening of electrons due to the polarizing influences of the surrounding fields. We can measure only the value for the whole molecule, and any attempt to consider a particular atom or group by not taking into consideration the variability of its value due to the influence of other atoms or groups in the molecule involves some uncertainty. Without disregarding the usefulness of the refractivity increments, it seems that, in many structural problems, a more logical approach to the interpretation of refractivity data should be based on considerations related to the molecule as a whole.

On the other hand, a comparison of the results

(1) K. Fajans, in A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 676; second edition, 1949, p. 1162.

(2) K. Fajans, *Chem. Eng. News*, **27**, 900 (1949); B. E. Cook, Thesis, University of Michigan, Ann Arbor, 1948.

(3) The bond system, theoretically superior to the atomic system, was recently discussed by B. C. Vickery and K. G. Denbigh, *Trans. Faraday Soc.*, **45**, 61 (1949); see also K. G. Denbigh, *ibid.*, **36**, 936 (1940).

obtained by the method of refractivity with other properties of molecules, like the Raman effect and the electric dipole moment, is very useful in the study of structural problems. In particular, Raman data are important in giving an indication of the variation of a particular bond through a large series of molecules and in showing how this particular bond is influenced by the other groups that a specific molecule contains.

Among recent studies on the general problem of the electronic structure of molecules, the work that is being developed by Fajans and collaborators⁴ is of particular importance in the interpretation of refractivity data. The extensive theoretical and experimental work carried on by this author⁵ since 1921 led to a new approach to the problem of chemical binding, the principles of which are outlined in the publications referred to above. It is one of the purposes of the present investigation to apply some of the ideas contained in Fajans' theory—the quanticule theory of molecular structure—to the interpretation of the refractivity of organic compounds.

In our previous papers,⁶ an attempt was made to review as completely as possible the literature concerning the refractivity of organic sulfur compounds, in particular aliphatic mercaptans and sulfides. The present work deals with the isomeric propyl and butyl mercaptans and contains a discussion of the electronic configuration of these molecules together with that of the corresponding propyl and butyl halides.

Experimental

Preparation of the Substances.—The *n*-propyl mercaptan for this work was a commercial product supplied by Eastman Kodak Company. The *n*-butyl mercaptan, also supplied by this Company (Eastman, "white label", no. 437, b. p. 96–98°), showed to be an azeotropic mixture with *n*-butyl alcohol. This mixture of minimum boiling point 94.55° (699.4 mm.) contained about 15% by weight of the alcohol⁷; d_{25}^{25} , 0.83193, $n_{D,25}^{25}$ 1.43370.

Isopropyl, isobutyl, s-butyl and t-butyl mercaptans were prepared according to the method described by Backer and Dijkstra⁸ by the condensation of the corresponding bromides with thiourea and subsequent saponification of the reaction product with a 5*N* sodium hydroxide solution. All bromides were dried and distilled just before starting the reaction. The isobutyl and *s*-butyl bromides were distilled under reduced pressure (about 160 mm.).

(4) K. Fajans, *et al.*, "Electronic Structure of Molecules," The University of Michigan, 35 p. mimeographed; see also ref. 2.

(5) K. Fajans, *Z. physik. Chem.*, **99**, 395 (1921); later work cited in refs. 1, 2, 4 and 17.

(6) Parts I and II of this series: S. Mathias, *Anais acad. brasil. cienc.*, **18**, 23 (1946); **20**, 287 (1948).

(7) Compare R. L. Kramer and E. E. Reid, *THIS JOURNAL*, **43**, 888 (1921).

(8) H. J. Backer and N. D. Dijkstra, *Rec. trav. chim.*, **51**, 290 (1932); H. J. Backer, *ibid.*, **54**, 215 (1935).

Purification of the Substances.—The purification of the mercaptans was done in two stages: (1) by changing the mercaptan into the lead mercaptide and liberating the mercaptan by decomposition of the mercaptide as described below, and (2) by submitting the product obtained to successive fractional distillations.

(1) The lead mercaptides were prepared according to the method described by Borgstrom, Ellis and Reid,⁹ by adding the mercaptan dissolved in ethyl alcohol to a 0.25 molar solution of lead acetate in a mixture of water and alcohol (1:1). After washing with a little ethyl alcohol, the precipitate was transferred to a round-bottomed flask and steam passed through the melted salt to remove the volatile materials. After cooling for a while, dilute hydrochloric acid was added, drop by drop, and the mercaptan formed was directly distilled from the flask. The distillate was transferred to a separatory funnel and the water removed. The mercaptan was then dried with anhydrous sodium carbonate and distilled.

(2) After treating as described above, the mercaptans were carefully fractionated in an atmosphere of dry nitrogen in an all-glass apparatus designed and built in this Laboratory. The apparatus had standard ground joints and a fractionating column 120 cm. long packed with glass spirals of the Widmer type. The column was protected against heat loss by a silvered vacuum jacket and could be made to operate under total reflux conditions. Controlled external heating was also used when required. The efficiency of the column, under atmospheric pressure, was determined by using a mixture of carbon tetrachloride and benzene¹⁰ and was found to correspond to about 22 theoretical plates. The apparatus could be operated either under atmospheric or reduced pressure, but no attempt was made to determine its efficiency under reduced pressure. A modified design of Todd's vacuum pressure regulator¹¹ was used to maintain a constant pressure during the distillations under reduced pressure. Calibrated thermometers of the Anschütz type, with the first graduations about 10 cm. above the lower end of the bulb, were immersed in a mercury cup 10 cm. deep, on the still head. With the aid of a magnifier, the temperature could be read to $\pm 0.02^\circ$. When operating under reduced pressure, the ground glass joints were tightly sealed with a suitable resin of high softening point. In order to detect the presence of traces of hydrogen sulfide, a filter paper impregnated with lead acetate was placed in a region next to the outgoing distillate.

The general method used in these fractionations can be illustrated with the case of *n*-propyl mercaptan:

First distillation: fraction 2, boiling range 64.75–64.80°; fraction 3, 64.80–65.00°; fraction 4, 65.00–65.05°; atm. pres. 695.3 mm.

Second distillation (redistillation of fraction 3): fraction 3a, boiling range 64.65–65.00°; fraction 3b, 65.00–65.07°; fraction 3c, 65.07–65.10°; atm. pres. 698.1 mm.

Third distillation (redistillation of fraction 3b): fraction 3b1, boiling range 65.05–65.10°; fraction 3b2, 65.10° constant; fraction 3b3, 65.10° constant; atm. pres. 701.0 mm.

Atmospheric pressures were measured with a precision standard barometer and reduced pressures with a mercury manometer and a cathetometer. All pressures reported are corrected for mercury expansion.

Only the middle fractions of the last distillations, showing a constant boiling point, were used for the physical measurements. These were started immediately after the obtention of the pure fraction.

Physical Measurements.—Densities were determined at 25° by means of pycnometers of the type described by

(9) P. Borgstrom, L. M. Ellis, Jr., and E. E. Reid, *THIS JOURNAL*, **51**, 3649 (1929); see also ref. 7.

(10) Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, 3rd ed., p. 82; Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1938, Ch. IV.

(11) F. Todd, *Anal. Chem.*, **20**, 1248 (1948).

Wibaut and collaborators.¹² Pycnometers of about 20 and 10 ml. capacity were used. They differed, however, from the pycnometers mentioned above in having longer capillaries with smaller internal diameters. These changes were made in order to decrease the loss by evaporation and to make negligible the correction for the vapor (the total vapor volume above the two marks was about 0.1 ml.). The distances between the marks and the meniscus of the liquid in the capillaries were measured to ± 0.01 mm. with the aid of a precision cathetometer. The temperature of the thermostat was kept constant to within $\pm 0.01^\circ$. The general technique followed was approximately the same as described by Bauer.¹³ From a large number of measurements, the uncertainty of these determinations was estimated to be $\pm 1.5 \times 10^{-4}$ g./ml. for the 20-ml. pycnometer and about twice as large for the 10-ml. pycnometer.

Refractive indices at 25.00 \pm 0.05° for eleven spectral lines were determined by means of a Pulfrich refractometer (Carl Zeiss, Jena, Germany). The instrument was calibrated by measuring the critical angle of emergence for pure water and for the following spectral lines:

Element	Wave length in Å.			
Helium	6678	5876	5016	4713 4471
Hydrogen	6563		4861	4340
Sodium		5893		
Mercury		5461		4358

The refractive indices of the prism for the spectral lines listed above were calculated by the equation

$$n_{25}^{\lambda}[P] = \sqrt{(n_{25}^{\lambda}[\text{H}_2\text{O}])^2 + \sin^2 \alpha_{\lambda}}$$

where $n_{25}^{\lambda}[P]$ is the refractive index of the prism at 25° for the wave length λ , $n_{25}^{\lambda}[\text{H}_2\text{O}]$ the refractive index of pure water at the same temperature and for the same wave length, and α_{λ} the corresponding critical angle of emergence measured in the instrument. For the refractive indices of pure water at 25°, the values of Tilton and Taylor¹⁴ were used. The refractive indices of the prism determined by this method agreed with the values indicated by the manufacturer to within one or two units in the fifth decimal place.

As the tables supplied with the instrument did not include the helium lines, the refractive indices for such lines were calculated by the equation

$$n_{25}^{\lambda} = \sqrt{(n_{25}^{\lambda}[P])^2 - \sin^2 \alpha_{\lambda}}$$

Results

Boiling points, densities and refractive indices for eleven spectral lines of highly purified samples of propyl and butyl mercaptans were determined. Tables I and II give the results obtained.

The molar refractivities calculated from these data are listed in Table III, which includes the values for infinite wave length determined by the reciprocal plotting method of Wulff¹⁵ based on the theory of dispersion (Fig. 1).¹⁶

Table IV gives the values for the molar refractivity, R_{5893}^{25} , the molar dispersivity,¹⁷ D , defined as $R_{5893} - R_{\infty}$, and the molar volume,

(12) J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff and J. Smittenberg, *Rec. trav. chim.*, **58**, 368 (1939).

(13) N. Bauer, "Determination of Density," p. 81, in A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945.

(14) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **20**, 419 (1938).

(15) P. Wulff, *Z. physik. Chem.*, **B21**, 368 (1933).

(16) The graphical extrapolations were made on the following scale: 1 mm. = 5×10^{-2} (cc./mole)⁻¹ = 0.1×10^{18} sec.⁻²

(17) N. Bauer and K. Fajans, *THIS JOURNAL*, **64**, 3023 (1942).

TABLE I
BOILING POINTS AND DENSITIES OF PROPYL AND BUTYL
MERCAPTANS

Mercaptan	B. p., °C.	Mm.	d^{25}_4
<i>n</i> -Propyl ^a	65.10	701.0	0.83598
Isopropyl ^b	49.90	697.0	.80895
<i>n</i> -Butyl ^c	96.10	701.7	.83679
Isobutyl	41.2	142	.82880
<i>s</i> -Butyl ^d	37.4	134	.82456
<i>t</i> -Butyl ^e	61.60	700.8	.79426

^a B. p. 67.4–67.6° (763 mm.), d^{25}_4 , 0.83572, Ellis and Reid, THIS JOURNAL, 54, 1674 (1932); d^{25}_4 , 0.8358, Selker and Kemp, *Ind. Eng. Chem.*, 36, 17 (1944). ^b 52.3–52.5° (753), d^{25}_4 , 0.80851, Ellis and Reid, *loc. cit.* ^c 98.6–99.0° (768), d^{25}_4 , 0.83651, Ellis and Reid, *loc. cit.* ^d d^{25}_4 , 0.82459, Ellis and Reid, *loc. cit.* ^e 63.7–64.2° (760), Rheinboldt, Mott and Motzkus, *J. prakt. Chem.*, 134, 268 (1932).

TABLE II
REFRACTIVE INDICES AT 25° OF PROPYL AND BUTYL
MERCAPTANS

Wave length, Å.	<i>n</i> -C ₃ H ₇ SH ^a	<i>i</i> -C ₃ H ₇ SH ^b	<i>n</i> -C ₄ H ₉ SH ^c	<i>i</i> -C ₄ H ₉ SH	<i>s</i> -C ₄ H ₉ SH ^d	<i>t</i> -C ₄ H ₉ SH
6678	1.43188	1.41836	1.43698	1.43272	1.43075	1.41678
6563	1.43227	1.41878	1.43739	1.43314	1.43111	1.41714
5893	1.43511	1.42154	1.44014	1.43582	1.43385	1.41984
5876	1.43515	1.42160	1.44021	1.43589	1.43391	1.41991
5461	1.43749	1.42387	1.44248	1.43814	1.43617	1.42216
5016	1.44072	1.42705	1.44562	1.44125	1.43929	1.42526
4861	1.44204	1.42839	1.44691	1.44256	1.44059	1.42654
4713	1.44349	0.42974	1.44832	1.44389	1.44196	1.42791
4471	1.44621	1.43246	1.45098	1.44655	1.44460	1.43057
4358	1.44767	1.43387	1.45237	1.44791	1.44608	1.43193
4340	1.44784	1.43419	1.45259	1.44815	1.44619	1.43216

^a n^{25}_{5893} 1.4351, Ellis and Reid, THIS JOURNAL, 54, 1677 (1932); n^{25}_{5893} 1.4353, Selker and Kemp, *Ind. Eng. Chem.*, 36, 17 (1944). ^b n^{25}_{5893} 1.4223, Ellis and Reid, *loc. cit.* ^c n^{25}_{5893} 1.4401, Ellis and Reid, *loc. cit.* ^d n^{25}_{5893} 1.4338, Ellis and Reid, *loc. cit.*

TABLE III
MOLAR REFRACTIVITIES AT 25° OF PROPYL AND BUTYL
MERCAPTANS

Wave length, Å.	<i>n</i> -C ₃ H ₇ SH	<i>i</i> -C ₃ H ₇ SH	<i>n</i> -C ₄ H ₉ SH	<i>i</i> -C ₄ H ₉ SH	<i>s</i> -C ₄ H ₉ SH	<i>t</i> -C ₄ H ₉ SH
∞	23.098	23.204	27.629	27.657	27.685	27.901
6678	23.623	23.742	28.235	28.265	28.296	28.539
6563	23.642	23.763	28.258	28.289	28.317	28.561
5893	23.777	23.900	28.414	28.441	28.474	28.724
5876	23.779	23.903	28.416	28.445	28.477	28.728
5461	23.890	24.016	28.543	28.573	28.606	28.862
5016	24.044	24.173	28.719	28.749	28.784	29.047
4861	24.106	24.240	28.791	28.823	28.858	29.125
4713	24.174	24.306	28.870	28.898	28.936	29.206
4471	24.304	24.441	29.018	29.049	29.087	29.364
4358	24.372	24.510	29.096	29.125	29.170	29.445
4340	24.381	24.526	29.108	29.139	29.176	29.459

V , of the compounds studied in this work. The Δ values represent the deviation from the corresponding value of the normal compound. It should be pointed out that the values for the molar dispersivity $R_{4471} - R_{6678}$, based on the very accurately measurable blue-violet and red lines of the helium spectrum are on the average larger by $0.0012 \approx 0.0010$ cc. than the extrapolated values of D . This close agreement in the case of six compounds indicates the reliability of the graph-

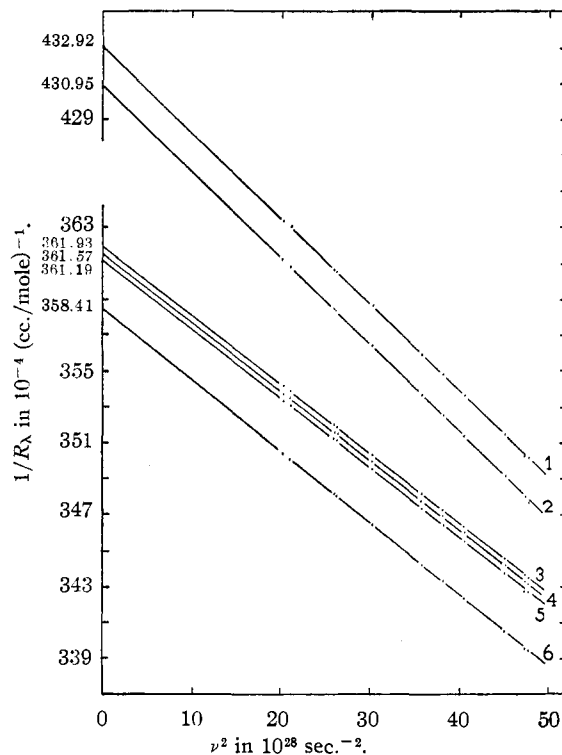


Fig. 1.—Extrapolations to infinite wave length of the molar refractivities of propyl and butyl mercaptans: 1, propyl; 2, isopropyl; 3, butyl; 4, isobutyl; 5, *s*-butyl; 6, *t*-butyl.

ical extrapolation. The positive signs of the Δ values of Table IV show that the molar refractivities, dispersivities and volumes are larger for the branched chains, the smallest deviation from the normal compounds occurring for the isobutyl, the largest for the tertiary butyl mercaptan.

Mercaptan	R_{5893}	ΔR_{5893}	D	ΔD	V	ΔV
<i>n</i> -Propyl	23.777	0.000	0.679	0.000	91.103	0.000
Isopropyl	23.900	+ .123	.696	+ .017	94.147	+3.044
<i>n</i> -Butyl	28.414	.000	.785	.000	107.776	0.000
Isobutyl	28.441	+ .027	.784	- .001	108.815	+1.039
<i>s</i> -Butyl	28.474	+ .060	.789	+ .004	109.375	+1.599
<i>t</i> -Butyl	28.724	+ .310	.823	+ .038	113.647	+5.871

The same order of variation is shown by the corresponding propyl and butyl halides (Table V).

Discussion

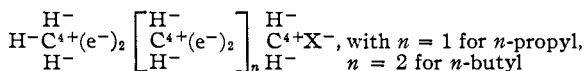
Quanticule Formulations.—Considering the views expressed by Fajans in his quanticule theory of molecular structure, several formulations are possible for some of the propyl and butyl mercaptans and halides, depending on whether the sign of the methylene groups alternates or not. Since no definite indication for an alternation is known at present for these compounds, we shall use here for the normal chain

TABLE V
 MOLAR REFRACTIVITY AND VOLUME OF PROPYL AND BUTYL HALIDES

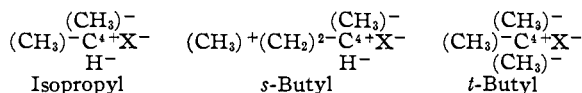
Chloride	B. p. °C. (760)	d_{15}^4	$n_{D_{15876}}^{15}$	R_{15876}^{15}	ΔR	V_{15}	ΔV
<i>n</i> -Propyl	46.60 ^a	0.89846 ^a	1.39142 ^d	20.790	0.000	87.420	0.000
Isopropyl ^b	34.8	.86797	1.38141	21.030	+ .240	90.490	+3.070
<i>n</i> -Butyl	78.50 ^c	.89197 ^b	1.40499 ^b	25.436	.000	103.780	0.000
Isobutyl ^d	68.85	.88290	1.40100	25.474	+ .038	104.847	+1.067
<i>s</i> -Butyl ^b	68.25	.87880	1.39975	25.522	+ .086	105.336	+1.556
<i>t</i> -Butyl ^e	50.7	.84739	1.38777	25.764	+ .328	109.240	+5.460
Bromide							
<i>n</i> -Propyl	70.97 ^f	1.35965 ^d	1.43700 ^d	23.701	0.000	90.466	0.000
Isopropyl	59.41 ^f	1.32223 ^d	1.42865 ^d	23.966	+ .265	93.026	+2.560
<i>n</i> -Butyl	101.60 ^g	1.28292 ^d	1.44241 ^d	28.284	.000	106.809	0.000
Isobutyl ^b	91.40	1.27197	1.43901	28.337	+ .053	107.729	+0.920
<i>s</i> -Butyl ^e	91.20	1.26808	1.43950	28.451	+ .167	108.059	+1.250
<i>t</i> -Butyl ^e	73.25	1.22861	1.43071	28.853	+ .569	111.531	+4.722
Iodide ^e							
<i>n</i> -Butyl	130.40	1.62366	1.50277	33.492	.000	113.344	0.000
Isobutyl	121.0	1.61176	1.49897	33.524	+ .032	114.181	+0.837
<i>s</i> -Butyl	120.0	1.60584	1.50269	33.859	+ .367	114.602	+1.258

^a Timmermans and Hennaut-Roland, *J. chim. phys.*, **29**, 529 (1932). ^b Timmermans and Martin, *ibid.*, **25**, 411 (1928).
^c Efring, thesis, Lund, 1938. ^d Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926). ^e Timmermans and Delcourt, *ibid.*, **31**, 85 (1934). ^f Skau and MacCullough, *THIS JOURNAL*, **57**, 2439 (1935). ^g Van Bogaert, *Bull. soc. chim. Belg.*, **36**, 384 (1927). ^h Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).

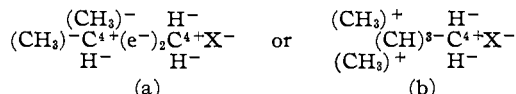
formulas which are near to the usual Lewis' formulations.



For the isopropyl, *s*-butyl and *t*-butyl compounds formulations analogous to that derived by Fajans and Cook² for the carbon tetralkyls $\text{C}^{4+}(\text{R}^-)_4$ will be assumed to be valid.



For the isobutyl compounds the following two alternatives may be considered



In all the above formulas $\text{X} = \text{SH}, \text{Cl}, \text{Br}, \text{or I}$.

Refractivities.—At the present stage of development of the quanticule theory it is not possible to arrive at a rigorous interpretation of the refractivity data given above. This theory permits one, however, to understand at least in a qualitative way that chain isomers differ with respect to refractivity. These differences cannot be brought into accord with the existing systems of additive increments.

Each of the given quanticule formulations contains a C^{4+} core and a more or less regular tetrahedral configuration of negative groups around this core. The observed differences in the properties of the isomers, as shown by Tables IV and V, must depend on the nature of these

groups, $(\text{e}^-)_2$, H^- , $(\text{CH}_3)^-$, $(\text{CH}_2)^2-$, and $(\text{CH})^3-$ and on their interactions with X^- , C^{4+} and with each other. While the attraction between C^{4+} and the negative groups causes the tightening of the latter and a decrease of refractivity, the repulsion between the negative quanticules themselves leads to their loosening and to an increase of refractivity. If one replaces by other quanticules the electron pair $(\text{e}^-)_2$ or the two H^- adjacent to C^{4+}X^- in the normal chains, the over-all refractivity can be expected to change. The fact that all ΔR values listed in Tables IV and V are larger for the bromides than for the corresponding chlorides shows that the over-all loosening caused by the branching becomes more pronounced with increasing size and polarizability of X^- . For a given X^- the ΔR values are larger when $(\text{e}^-)_2$ and both H^- are replaced by the larger $(\text{CH}_3)^-$ quanticules in the *t*-butyl than when $(\text{e}^-)_2$ and only one H^- are replaced by other groups in the isopropyl and *s*-butyl compounds.

In the isobutyl compounds the ΔR values are relatively small (0.03–0.05 cc.). Correspondingly the negative quanticules attached to C^{4+}X^- differ in formula (b) from those in the normal chain only by the replacement of $(\text{e}^-)_2$ by $(\text{CH})^3-$ while in the alternative formula (a), as in the normal chains, C^{4+}X^- is connected with $(\text{e}^-)_2$ and two H^- .

Thus it seems that the interaction of the negative groups among themselves and with the C^{4+} cores which they surround is the preponderant factor.¹⁸ The increase in size and polarizability of these groups produces an increase in the over-all loosening effect.

(18) See ref. 6, Part II, p. 305.

The above-mentioned increase of the ΔR values with the polarizability of X^- does not apply to the comparison of $(SH)^-$ with the halide quanticules. The molar refractivities (5876 Å.) of the *n*-propyl and *n*-butyl mercaptans (at 25°) are by 0.10 ± 0.03 cc. larger than those of the bromides (at 15°). This indicates that the electronic polarizability of $(SH)^-$ is in these compounds somewhat larger than that of Br^- . Nevertheless, the ΔR values of the isomeric mercaptans are distinctly smaller even than those of the chlorides. One has to conclude that the difference in the symmetry of the fields of the cores S^{6+}, H^+ on the one hand and of Cl^{7+} on the other hand is also of importance for the mutual loosening and tightening effects in which $(SH)^-$ and Cl^- are involved. This is similar to the differences in behavior between $(NH_4)^+$ and alkali ions.¹⁹

Although in general² the variations in the values for the molar volume are parallel to those of the molar refractivity, the ΔV values in Table V are smaller for the bromides than for the chlorides, the latter being nearly equal to those of the mercaptans.

Dipole Moments.—The points of view discussed above can be applied to other properties of chain isomers. Values for the dipole moments of isomeric propyl and butyl mercaptans were not found in the literature and their determination is being carried out in this laboratory. However, data are available for the corresponding halides and were discussed by Wheland²⁰ on the basis of the resonance theory. He used the results of Wiswall and Smyth on vapors.²¹ More complete are the data of Parts²² on solutions in benzene, but they are influenced by the interaction between solute and solvent. Since all available measurements were performed at one temperature only, they do not allow a reliable correction for the atomic polarization. Thus it suffices to mention here the following conclusions based on the apparent dipole moments given by Parts. The values of μ in debyes for isobutyl chloride (1.96), bromide (1.97) and iodide (1.87) agree within the experimental errors with those for the normal compounds, as could be expected especially on the basis of formula (a). The moments of isopropyl and *s*-butyl compounds are larger than those of the normal ones, the values of $\Delta\mu$ being 0.11 for the chlorides, 0.15 for the bromides and iodides. The $\Delta\mu$ values of *t*-butyl are 0.18 for the chlorides, 0.25 debye for the bromides and iodides.

One can conclude that in general the gradation of the apparent dipole moments goes parallel to

(19) See K. Fajans and O. Johnson, *THIS JOURNAL*, **64**, 668 (1942).

(20) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 123.

(21) R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

(22) A. Parts, *Z. physik. Chem.*, **B7**, 327 (1930); **B12**, 312 (1931).

that of the electronic polarization given by the ΔR values. This can be understood since the loosening of the electronic system of X^- can be expected to be the result of an increase of the internuclear C^4+X^- distance and thus of a smaller degree of deformation of X^- .

Stretching Frequencies.—Further information about the structure of these molecules is given by a consideration of the frequency values ν obtained from Raman spectra and usually assigned to the stretching of the C—X bond ($X = SH, Cl, Br, \text{ or } I$). Table VI gives the ν values selected by Kohlrausch. The $\Delta\nu$ values

TABLE VI
C—X STRETCHING FREQUENCIES ν IN PROPYL AND BUTYL MERCAPTANS AND HALIDES^a

Mer- captan	ν (in cm. ⁻¹)	$\Delta\nu$	Bromide	ν (in cm. ⁻¹)	$\Delta\nu$
<i>n</i> -Propyl	651	0	<i>n</i> -Propyl	563	0
Isopropyl	626	-25	Isopropyl	536	-27
<i>n</i> -Butyl	653	0	<i>n</i> -Butyl	561	0
(Isobutyl	668 or 708 ?)		(Isobutyl	621 or 653 ?)	
<i>s</i> -Butyl	617	-36	<i>s</i> -Butyl	533	-28
<i>t</i> -Butyl	587	-66	<i>t</i> -Butyl	515	-46
Chloride			Iodide		
<i>n</i> -Propyl	648	0	<i>n</i> -Propyl	502	0
Isopropyl	612	-36	Isopropyl	489	-13
<i>n</i> -Butyl	653	0	<i>n</i> -Butyl	504	0
(Isobutyl	689 or 726 ?)		(Isobutyl	582 or 602 ?)	
<i>s</i> -Butyl	609	-44	<i>s</i> -Butyl	490	-14
<i>t</i> -Butyl	570	-83	<i>t</i> -Butyl	487	-17

^a K. W. F. Kohlrausch, "Ramanspektren," Akademische Verlagsgesellschaft, Leipzig, 1943, p. 240-243.

in the table show that, with the exception of the isobutyl compounds, the frequencies are smaller for the branched chain isomers than for the normal ones and that ν decreases for the butyl compounds in the same order, *n*-butyl, *s*-butyl, *t*-butyl, in which the refractivities, dispersivities, molar volumes and apparent dipole moments increase.

In the case of the isobutyl compounds two frequencies are given in Table VI since it is not clear which of them should be assigned to the C—X bond.²³ This and the fact that the resulting $\Delta\nu$ values are partly much larger for the isobutyl compounds than for the other isomers, contrary to the behavior of other properties treated in this paper, make it advisable to leave the uncertain ν values of the isobutyl compounds out of discussion.

In order to interpret the difference between the ν values of the other isomers, one may assume a simplified model of the molecules RX as made up of the components R^+ and X^- vibrating against each other. In the equation

$$\nu = (1/2\pi c)\sqrt{k/\bar{\mu}}$$

for a harmonic oscillation, the reduced mass $\bar{\mu}$

(23) Compare I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 485 (1946).

is the same for isomers. Thus, the consideration of the ν values of Table VI leads to a comparison of the force constants k of the isomers. The force constants involved in these stretching vibrations can be used as a measure of the strength of the binding between X^- and R^+ .

This binding is the resultant of the attraction exerted on X^- by C^{4+} and the repulsion due to the other three negative groups surrounding the latter. Hence, the same factors which were assumed to cause an increase of refractivities and dipole moments of isomers can, on the basis of these simplified deductions, be expected to lead to the observed diminution of the stretching frequencies.

The analogy in the gradation of different properties is, however, not complete. For instance, the ΔR values of the bromides are larger, but their absolute $\Delta\nu$ values are smaller than the corresponding values of the chlorides. It is premature to attempt a clarification of these details, but a general remark should be added here.

Fajans⁵ recognized in 1921 that the difference in properties of chain isomers cannot be understood if one considers merely interactions within bonds connecting two adjacent atoms and that forces between more remote atoms have also to be taken into account. Now, on the basis of the quanticule formulations, it is evident that the

force between C^{4+} and X^- depends on the nature of the other three R^- groups. And *vice versa*, the properties of $(R^-)_3C^{4+}$ depend on the nature of X^- due to the coulombic forces as well as to mutual polarization effects. Thus it is not surprising to find that the complicated interactions among the quanticules do not influence different properties of isomers in an identical manner.

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Summary

Densities and refractive indices, at 25°, for eleven spectral lines, of highly purified samples of the isomeric propyl and butyl mercaptans were determined.

From the results obtained, the molar refractivities, dispersivities and volumes were calculated. The extrapolated values for R_∞ were derived by the graphical method of Wulff.

An attempt was made to correlate these data, and those for analogous isomeric halides, as well as dipole moments and Raman frequencies, from the point of view of the quanticule theory of molecular structure.

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[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES]

The Alleged Complexity of Solid Aluminum Chloride

BY L. M. FOSTER

The complex nature of solid aluminum chloride was reported by Smits and Meijering.¹ In brief, their observations were as follows: 1. By fractionally subliming pure solid aluminum chloride, a residue could be obtained which had a vapor pressure as much as 50% lower than the equilibrium vapor pressure at the same temperature. 2. By rapidly condensing aluminum chloride vapor, a solid condensate could be obtained which had a vapor pressure considerably higher than the equilibrium pressure. 3. The vapor pressure of these residues and condensates always reverted to the normal equilibrium values on long standing at constant temperature. 4. A "distorted" phase obtained as in 1, was observed to melt several degrees higher than the accepted melting point of aluminum chloride (192.6°). Once the material melted, its vapor pressure immediately reverted to the normal value for that temperature. 5. Only one phase could be detected by X-ray examination of solid aluminum chloride.

(1) A. Smits and J. L. Meijering, *Z. physik. Chem.*, **B41**, 98-111 (1938); see also A. Smits, "Die Theorie der Komplexität und der Allotropie," Verlag Chemie, Berlin, 1939, lithographed by Edwards Brothers, Inc., Ann Arbor, Michigan, 1944.

The explanation offered by Smits and Meijering for this anomalous behavior was that pure solid aluminum chloride is a mixture of two "pseudo-phases," each of which has a characteristic vapor pressure.

With the exception of Smits and Meijering's vapor pressure work, no measurement on aluminum chloride has indicated the possibility of separating the substance into two forms.²

The purpose of the present investigation was to extend the work of Smits and Meijering and to seek an explanation for the anomalous behavior they reported.

Experimental

Materials.—The aluminum chloride used for the vapor pressure measurements was made by the reaction of pure hydrogen chloride gas at about 400° with 99.99% aluminum contained in a pure alumina boat. The hydrogen chloride was made by adding concentrated hydrochloric acid dropwise to concentrated sulfuric acid. The gas was dried by passing it over phosphorus pentoxide. The

(2) The "International Critical Tables," Vol. 5, p. 98, and a number of handbooks, list alpha and beta forms of aluminum chloride having different specific heats. This was an editorial error, however. The reference cited dealt with ammonium rather than aluminum chloride.