

On the Stable Relative Orientation of Groups Connected by a Carbon-Carbon Single Bond

VERNER SCHOMAKER AND D. P. STEVENSON

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

(Received June 17, 1940)

LANGSETH and his co-workers¹ have recently applied the results of essentially incomplete spectroscopic studies of liquid cyclohexane, symmetrical tetrachloroethane, and ethylene deuterobromide to a discussion of the intramolecular forces restricting internal rotation about the C—C bond. We believe that none of their structural conclusions is correct. Their discussion is based on their conclusion that in these molecules the opposed or eclipsed configurations are the stable ones. Insofar as liquid cyclohexane and symmetrical tetrachloroethane are concerned this conclusion is most probably incorrect since it directly contradicts the results of a great number of essentially more straightforward studies of these and similar molecules in the gaseous and solid phases, and since it is probable that molecules in the liquid generally have structures closely related to those in the gas and the solid, at least when these are not too different. But whatever may be the structures of these molecules in the liquid, it is certainly true that the structures of the free molecules are more pertinent to a discussion of intramolecular forces. These structures indicate that there is a general tendency for the staggered configurations to be the stable ones, and Langseth's general discussion^{1c} must accordingly be without significance. Some of the existing evidence on cyclohexane, symmetrical tetrachloroethane, and related molecules is briefly given below together with a preliminary report on an electron diffraction investigation of the structure of gaseous symmetrical tetrachloroethane. We know of no direct evidence regarding the stable configuration of the ethyl bromide molecule. We believe, however, that in ethyl bromide and in ethane it is the staggered configuration which is the more stable, as it is in the hydrocarbons and substituted hydrocarbons for which unambiguous

¹ a. A. Langseth and B. Bak, *J. Chem. Phys.* **8**, 403 (1940). b. A. Langseth and H. J. Bernstein, *ibid.* **8**, 410 (1940). c. A. Langseth, H. J. Bernstein and B. Bak, *ibid.* **8**, 415 (1940). d. A. Langseth, H. J. Bernstein and B. Bak, *ibid.* **8**, 430 (1940).

structural information exists. It seems likely therefore that Langseth's assignments of the two isomeric components^{1d,2} of the C—Br stretching frequency of ethylene deuterobromide should be reversed.

X-ray studies of crystalline cyclohexane,^{3a} β -benzene hexabromide and hexachloride,^{3b} and 1,4-di-iodocyclohexane^{3c} uniformly eliminate the possibility of the planar cyclohexane ring, proposed by Langseth and Bak, as does the electron diffraction investigation of gaseous cyclohexane by Pauling and Brockway.⁴ Beach and his co-workers⁵ have found staggered configurations for ethylene chloride, chlorobromide, and bromide, and 1,1,2-trichloroethane as we have for the 2,3-dibromobutanes and propylene bromide. Klug reported crystalline ethylene iodide⁷ to have a *trans* and thus staggered configuration.

Our electron diffraction photographs⁸ of gaseous symmetrical tetrachloroethane were obtained

TABLE I.

MAX.				MIN.			
MAX.	MIN.	C_n	S_0	MAX.	MIN.	C_n	S_0
1	1	-3	1.61	6	7	12	11.85
		5	2.63			-10	12.74
2	2	-7	3.68	7	8	9	13.64
		10	4.74			-4	14.38
3	3	-5	5.54	8	9	6	15.54
		3	6.14			-8	16.72
4	4	-11	6.77	9	10	7	17.97
		12	7.68			-2	18.70
5	5	-5	8.47	10	11	3	19.54
		5	9.43			-6	20.55
	6	-13	10.54	11		5	21.85

² M. de Hemptinne and C. Velghe, *Physica* **5**, 958 (1938).

³ a. O. Hassel and H. Kringstad, *Tidskr. Kemi. Bergvesen*, **10**, 128 (1930). b. R. G. Dickinson and C. Blicke, *J. Am. Chem. Soc.* **50**, 764 (1928). c. E. Holmøy and O. Hassel, *Zeits. f. physik. Chemie* **B16**, 234 (1932).

⁴ L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **59**, 1223 (1937).

⁵ a. J. Y. Beach and K. J. Palmer, *J. Chem. Phys.* **6**, 639 (1938). b. J. Y. Beach and A. Turkevich, *J. Am. Chem. Soc.* **61**, 303 (1939). c. A. Turkevich and J. Y. Beach, *ibid.* **61**, 3127 (1939).

⁶ a. D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.* **61**, 3173 (1939). b. V. Schomaker and D. P. Stevenson, unpublished observations.

⁷ H. P. Klug, *Zeits. f. Krist.* **90**, 495 (1935).

⁸ L. O. Brockway, *Rev. Mod. Phys.* **8**, 231 (1936).

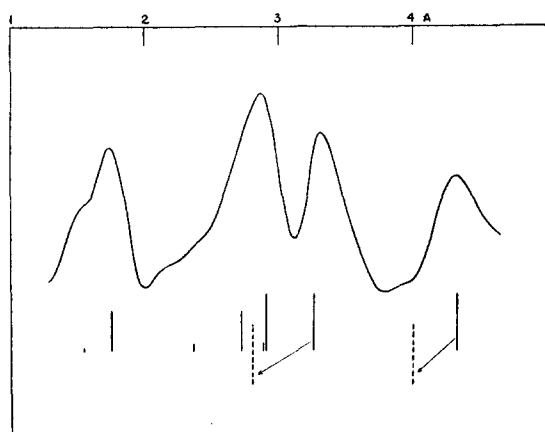


FIG. 1. The radial distribution function for symmetrical tetrachloroethane. The solid vertical lines give the interatomic distances to be expected for a molecule with bond distances and angles as in ethyl chloride and methylene chloride. The lengths of the lines indicate the relative importance of the distances in the scattering formula for the more symmetrical (C_{2h}) model. For the less symmetrical staggered model (C_2) the 3.25Å line would become three times as long as the 4.31Å line. The dotted lines correspond to the orientation-dependent distances in the symmetric (C_{2v}) eclipsed model; for the C_2 eclipsed model the longer of these distances becomes three times as important as the shorter one. The arrows relate the corresponding orientation-dependent distances of the two types of models.

from a sample (b.p. $142.8 \pm 0.1^\circ$) which was part of the middle fraction obtained on distilling a large quantity of Eastman symmetrical tetrachloroethane through a 25-cm helix packed column with controllable reflux ratio. The photographs were taken with the high temperature nozzle.⁹ The temperature of the boiler was varied from 70° to 120° . The wave-length of the electrons was 0.0615Å (a_0 for gold, 4.070Å) and the camera distance was 10.85 cm.

The photographs showed eleven rings whose measured s values ($s = (4\pi/\lambda) \sin(\vartheta/2)$) are given in Table I along with the coefficients C_n of the radial distribution function.¹⁰ Characteristic features of the diffraction pattern are the relatively weak third and fifth maxima, the broad appearance of the eighth and the shelf-like nature of the tenth maximum.

The radial distribution function shown in Fig. 1 has maxima at 1.74, 2.86, 3.31 and 4.32Å. The first of these (1.74Å) corresponds to the

carbon-chlorine bond distance (1.76Å), and the second (2.86Å) to an unresolved average of the nonbonded carbon-chlorine distance (2.74Å in ethyl chloride^{11a}) and the distance between chlorine atoms bound to the same carbon atom (2.92Å in methylene chloride^{11b}). The positions of the other two maxima at 3.31Å and 4.32Å correspond to the chlorine-chlorine distances (3.25Å and 4.32Å) which would be expected if the bond distances and bond angles are the same as the corresponding distances and angles in ethyl chloride and methylene chloride and if the molecule has one (or both) of the "staggered" relative orientation of the two $-\text{CHCl}_2$ groups about the C—C bond. Moreover, it may be seen from Fig. 1 that these peaks are in complete disagreement with the distances to be anticipated for the "opposed" configuration proposed by Langseth and Bernstein.^{1b} The peaks of the radial distribution function which depend on the relative orientation of the two ends of the molecule are quite narrow. It therefore seems likely that the molecules are fairly rigid. In particular, the sharpness of the 3.31Å peak indicates that the amplitude of libration is less than that ($15\text{--}20^\circ$) which has been estimated for ethylene chloride, etc.^{5,6} The approximate 3 : 2 ratio of the heights of the 3.31Å and 4.32Å peaks of the radial distribution function suggest that the gas at the temperatures of our experiments consist of a roughly equimolar mixture of the two staggered isomers. We believe that the complete treatment of our data by the correlation method will provide a more precise estimate of the relative abundance of the two isomers as well as the answer to the rather large discrepancy between the position of the 3.31Å peak of the radial distribution function and the value calculated from our model. Our tentative conclusions regarding the relative abundance and rigidity of the isomers are in good agreement with those of Smyth and McAlpine¹² from dipole moment measurements on the gas.

We are indebted to Professor Linus Pauling for helpful counsel about the matters discussed in this paper.

⁹ L. O. Brockway and K. J. Palmer, *J. Am. Chem. Soc.* **59**, 2181 (1937).

¹⁰ a. L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **57**, 2684 (1935). b. Verner Schomaker, American Chemical Society Meeting, Baltimore, Maryland, April, 1939.

¹¹ a. J. Y. Beach and D. P. Stevenson, *J. Am. Chem. Soc.* **61**, 2643 (1939). b. L. E. Sutton and L. O. Brockway, *ibid.* **57**, 479 (1935).

¹² C. P. Smyth and K. B. McAlpine, *J. Am. Chem. Soc.* **57**, 979 (1935).