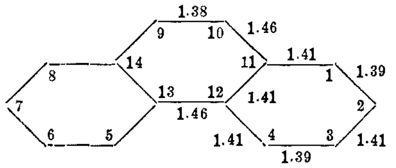
For phenanthrene the five unexcited structures lead to $^{4}/_{5}$ double bond character for the 9–10 bonds, $^{3}/_{5}$ for the 1–2 bonds, $^{2}/_{5}$ for the 1–11, 11–12 and 4–12 bonds, and $^{1}/_{5}$ for the 10–11 and 12–13 bonds, and the predicted configuration is



Similar prediction can be made for larger molecules. It must be pointed out that the contributions of excited structures become important for bonds with small double bond character, inasmuch as in conjugated systems excited structures alone may lead to as much as 20% double bond character; it is probable that the maximum carbon–carbon bond distance in aromatic hydrocarbons is about 1.46 Å., the minimum being the double bond distance 1.38 Å.

The predicted average interatomic distance is 1.41 Å. in naphthalene, anthracene and phenanthrene, this value being somewhat larger than the benzene value (1.39 Å.). With increase in size of the hydrocarbon the carbon–carbon distances should all approach the graphite value 1.42 Å.

The only experimental values of sufficient accuracy to permit a test of the predicted values are those obtained by Robertson in his careful and thorough x-ray investigations of the structure of crystals of naphthalene[17] and anthracene.[18] In each of these molecules Robertson reports the value 1.41 Å. for the average carbon–carbon bond distance, in complete agreement with the predicted value.[19] He does not discuss individual variations from the average; however, measurements made on his reproduced electron distribution projections (Fig. 2 for naphthalene, Fig. 2 for anthracene) show differences of 2 or 3% in the predicted directions.[20]

Summary

Using experimental values for carbon–carbon bonds, a function is plotted showing the dependence of interatomic distance on bond character for single bond–double bond resonance. This function is tested with data for other bonds, and used in the discussion of the electronic structure of molecules containing conjugated double or triple bonds or aromatic nuclei and of molecules containing carbon–chlorine bonds adjacent to double bonds. The dependence of bond angles on single bond–double bond resonance is discussed. Values of carbon–carbon bond distances in polynuclear aromatic hydrocarbons are predicted and compared with the existent experimental data.

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[17] J. M. Robertson, *Proc. Roy. Soc.* (London), **A142**, 674 (1933).

[18] J. M. Robertson, *ibid.*, **A140**, 79 (1933).

[19] The data for chrysene [J. Iball, *ibid.*, **A146**, 140 (1934)] are also compatible with this value.

[20] The value 1.41 Å. has also been reported for the carbon–carbon distance in benzene derivatives. We think it probable that this is 0.02 Å. too large.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM THE ONTARIO RESEARCH FOUNDATION]

Vapor Pressures of Certain Glycols

BY O. J. SCHIERHOLTZ AND M. L. STAPLES

In connection with other current research work, the authors have had occasion to determine the vapor pressure curves for the following glycols: ethylene, 1,2-propylene, 1,3-propylene, 1,3-butylene and 2,3-butylene.

A search of the literature for physical constants of these compounds revealed the fact that comparatively little has been published. With the exception of ethylene glycol, no vapor pressure data could be found, and many of the physical constants which are recorded are not at all concordant. The densities and refractive indices have been determined for all the above glycols, and are tabulated below.

All the compounds used in the determinations were purified by distillation, suitable neutralizing agents being used to obtain completely neutral, colorless, odorless products. The purities were such that the refractive index of successive fractions did not differ by more than 0.00038, and in most cases the difference was considerably less.

The starting materials for those glycols not synthesized in this laboratory were as follows: ethylene glycol and 1,2-propylene glycol, Carbide and Carbon Chemicals Corporation; 1,3-propylene glycol, Eastman Kodak Company.

Preparation of 2,3-Butylene Glycol.—This compound was prepared by the hydrolysis of 2,3-dibromobutylene, $CH_3CHBrCHBrCH_3$ (Eastman, b. p. 155–157°) in the presence of lead oxide. A similar method has been used by Dr. Harold Hibbert of McGill University, in the synthesis of a number of polyhydroxy compounds.

The following procedure was used: 30 cc. of 2,3-dibromobutylene and 300 g. of finely ground lead oxide were agitated in 2 liters of water for twenty-four hours at room temperature, with a high-speed stirrer. The precipitated lead bromide and excess lead oxide were then filtered off and the liquid concentrated under vacuum to about 500 cc. By chilling with ice, as much as possible of the lead bromide still in solution was precipitated and removed by filtration. To remove any lead remaining in solution, the filtrate was treated with hydrogen sulfide. After filtering, the liquid was further concentrated in the presence of a small amount of silver carbonate, to eliminate the last traces of halogen. The yield of glycol obtained was 50% of the theoretical. Prompt reaction of any liberated hydrogen bromide with the lead oxide seems to be essential to obtain good yields. Efficient agitation is an aid to this end. With the same point in view, the use of freshly precipitated lead hydroxide has been advocated.

Preparation of 1,3-Butylene Glycol.—The synthesis of this compound was carried out by using a slight modification of the method described by Halpern.[1] The procedure consisted of the reduction of acetaldol with aluminum amalgam. In the present case, 200 cc. of acetaldol (Eastman, Tech.) was distilled at 20 mm. pressure into 2 liters of water, in order to avoid the usual strongly exothermic reaction which is noted in the receiver when aldol is distilled alone. The solution was further diluted to 3.5 liters and cooled to 18°. Aluminum amalgam was then added at intervals to avoid rise in temperature, and the mixture allowed to stand for three days in order to complete the reaction. A yield of 75% of the theoretical amount of glycol was finally obtained.

Method of Determining Vapor Pressures.—The vapor pressures were studied by boiling the liquid under different pressures. The apparatus consisted of a Claisen distilling flask with a specially wide side-arm bent down at right angles and attached, by means of an adapter, to a receiver which was packed in ice. A cone-type electrical heater was placed under the distilling flask, and the whole assembly mounted on a shaking machine of the reciprocating type.

With the use of agitation, practically all superheating was overcome, as indicated by the difference between the liquid and vapor temperatures which was found to be of the order of about 0.5°. The vapor temperatures were determined by a short-range type precision thermometer. With this type of thermometer, the mercury column was surrounded completely by vapor, and stem corrections were avoided. The usual practice of bleeding a fine stream of air into the boiling liquid, in order to overcome bumping, could not be used, for this was shown to produce a considerable effect on the boiling point. Constant pressures were obtained by including a 10-liter chamber in the apparatus train, and using a pressure regulator.[10] The temperatures were determined to an accuracy of 0.1°, while the pressures could be read to 0.3 mm. All pressures are recorded in mm. of mercury at 0°.

TABLE I

PHYSICAL CONSTANTS OF THE GLYCOLS

Source of data	B. p., °C. (760 mm.)	Refr. index n_D	°C.	Density d_4	°C.
		Ethylene			
Taylor and Rinkenbach[2]	197.2			1.1132	20
Karvonen[3]		1.43178	20		
Authors	197.2	1.43192	20	1.1140	20
		1.43072	25		
		1,2-Propylene			
Wurtz[4]	188–189			1.051	0
Authors	187.4	1.43162	25	1.0354	23
		1,3-Propylene			
Rayner[5]	210–211			1.0554^{20}	20
Karvonen[3]		1.43983	20	1.0597	20
Wurtz and Reboul[6]	216			1.053	19
Authors	214.7	1.43847	25	1.0538	20
		1.43940	21		
		1,3-Butylene			
Bergmann, Miekeley and von Lippmann[7]	108–109(12)	1.4418	19.5		
Wurtz[8]	207–208(769)			1.0259	
Authors	207.5	1.44252	19.5	1.0053	20
		1.44098	25		
		2,3-Butylene			
Kling[9]	178–180				
Wurtz[4]	183–184			1.048	0
Authors	182.5	1.43637	25	1.0033	20

TABLE II

VALUES FOR GLYCOLS

Temperature range, °C.	Constant A	Constant B
	Ethylene	
90–130	3193.6	9.7423
130–197.2	2994.4	9.2477
	1,2-Propylene	
80–130	3039.0	9.5157
130–187.5	2925.2	9.2317
	1,3-Propylene	
110–160	3305.4	9.6951
160–214.7	3154.9	9.3484
	1,3-Butylene	
100–150	3116.7	9.3890
150–207.5	3035.6	9.1979
	2,3-Butylene	
80–130	3023.9	9.5521
130–182.5	2907.1	9.2616

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(1) Halpern, *Monatsh.*, **22**, 63 (1901).

(2) Taylor and Rinkenbach, *Ind. Eng. Chem.*, **18**, 676 (1926).

(3) Karvonen, *Ann. Acad. Sci. Fennicae*, **A10**, No. 10, 9 (1918).

(4) Würtz, *Ann. chim. phys.*, [3] **55**, 438–454 (1859).

(5) A. Rayner, *J. Soc. Chem. Ind.*, **45**, 265–266, 287–288T (1926).

(6) Wurtz and Reboul, *C. E.*, *Compt. rend.*, **79**, 169 (1874).

(7) Max Bergmann, A. Miekeley and E. von Lippmann, *Ber.*, **62**, 1467–1474 (1929).

(8) Wurtz, *Bull. soc. chim.*, [2] **41**, 362 (1884).

(9) A. Kling, *Ann. chim. phys.*, [8] **5**, 553 (1905).

(10) O. J. Schierholtz, *Ind. Eng. Chem., Anal. Ed.*, **7**, 284 (1935).

Experimental Results

In the case of each compound, determinations were made at from twelve to fifteen different pressures over the range 10–760 mm. By plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature, an almost straight line relationship was obtained. The constants for the conventional equation

$$\log_{10} p_{\text{mm.}} = -(A/T) + B$$

were evaluated, and are recorded in Table II. Vapor pressures calculated by means of this equation fall within the limit of error of the experimental results.

Summary

1. The vapor pressure curves over the range 10–760 mm. have been determined for the following glycols: ethylene, 1,2-propylene, 1,3-propylene, 1,3-butylene and 2,3-butylene. With the exception of ethylene glycol, these data are here reported for the first time.

2. The densities and refractive indices are given for all the above compounds.

3. The methods used for the preparation of 1,3-butylene and 2,3-butylene glycols are also described.

TORONTO, CANADA RECEIVED JUNE 28, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Mercury–Mercuric Oxide–Saturated Barium Hydroxide and Calcium Hydroxide Electrodes

BY G. J. SAMUELSON AND D. J. BROWN

It was the purpose of this research to study the mercury, mercuric oxide, barium hydroxide electrode with a view to its being used as a reference electrode. A saturated solution of the base was used to avoid troublesome preparation of standard solutions, thus permitting of easier preparation than is possible with the unsaturated type. Brown and Andrews[1] used Ming Chow's[2] electrode, containing sodium hydroxide, as a standard in their work and found its use very satisfactory.

The cell studied was, according to the common convention in designating it, as follows

$$Hg/(HgO(s), Ba(OH)_2(s)/m\ KCl/KCl(s), Hg_2Cl_2(s)/Hg$$

In the spontaneous reaction within the cell, an electron current flows in the external circuit from left to right, the complete reaction being

$$Hg + Ba(OH)_2 + Hg_2Cl_2 \rightleftharpoons 2Hg + BaCl_2 + HgO + H_2O$$

Mercuric Oxide.—Mercuric oxide was prepared by decomposing pure mercuric nitrate. However, electrodes containing this oxide gave potentials not differing sensibly from those obtained with half-cells containing "chemically pure" commercial mercuric oxide.

Barium Hydroxide.—The best available grade of barium hydroxide was recrystallized from distilled water.

Potassium Chloride.—This was prepared by recrystallization of "chemically pure" potassium chloride from distilled water.

Mercurous Chloride.—Calomel was prepared electrolytically by the method of Lipscomb and Hulett.[3]

Agar-Agar.—This was an ordinary commercial form of the substance.

Water.—The water used was twice distilled, once from alkaline permanganate, Pyrex containers and a block-tin condenser being employed.

Electrode Vessels.—Electrode vessels similar to type to those of Lewis, Brighton and Sebastian.[4]

Reference Half-Cell.—A layer of mercury in the chamber was covered with a layer of electrolytically prepared calomel containing crystals of potassium chloride. Over this was poured a saturated solution of potassium chloride to within a few centimeters of the top of the chamber.

Experimental Half-Cells.—A flask containing water and excess barium hydroxide and mercuric oxide was shaken frequently, the contents of the flask being kept near the temperature at which measurements were to be made. This mixture was poured into the electrode chamber in which were a layer of mercury and additional barium hydroxide and mercuric oxide.

Half-Cell Chamber.—A glass jar, 6 cm. in diameter and similar to a hydrometer jar, was nearly filled with a saturated solution the same as that used in the electrode, excess of the solute being added. The jar was fitted with a large rubber stopper. The lower part of the long straight arm of an h-shaped glass tube passed through the large rubber stopper and dipped into the solution within the jar. The bent side-arm of the tube passed through a one-holed rubber stopper which was inserted into the mouth of the electrode vessel, the tube dipping beneath the surface of the solution in the vessel. The arrangement was such that the small stopper and h-tube suspended the electrode vessel in a position parallel to the jar, and on about the same

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[1] Brown and Andrews, THIS JOURNAL, **42**, 488 (1920).

[2] Ming Chow, *ibid.*, **56**, 388 (1934); **57**, 254 (1935).

[3] Lipscomb and Hulett, *ibid.*, **38**, 22 (1916).

[4] Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).