The author[3] recently showed that for carbon-carbon bonds the points of plot of E, the bond-energy in kcal., against the bond-order N lie on the parabola

$$(1 - N/4)^2 = 1 - E/133 \qquad (3)$$

The fact that the number four appears as a constant associated with N may be of significance since this is the theoretical maximum bond-order for carbon–carbon bonds as well as being the number of carbon valence electrons.

By eliminating N from (1) and (3) we obtain the equation

$$D = a + b\left(\frac{n - 1/2}{n + 1/2}\right)^{\gamma} \qquad (4)$$

where $\gamma = 4 - 4\sqrt{1 - E/133}$, relating E and D for carbon–carbon bonds. The numerical values[1] of a, b and n are 1.015, 0.875 and 2, respectively.

Inspection of the points of plot of E against D for C—C, C=C, and C≡C bonds (58.6, 100, 123 kcal. and 1.54, 1.33, and 1.204 Å., respectively)[1,3] shows that the relation is very nearly linear. Cherton[4] has given a simple linear expression relating these variables. If we assume that this relationship is actually linear, then by setting

$$E = p(r - D) \qquad (5)$$

in (3) we derive a relation between N and D for carbon–carbon bonds of quite a different type from (1) which relates these same variables. Using the known values of D for C—C, C=C and C≡C bonds we find from (3) and (5) that[5]

$$(1 - N/4)^2 = 1.488(D - 1.162) \qquad (6)$$

and

$$E = 197.9(1.834 - D) \qquad (7)$$

The curves represented by (1) (for carbon-carbon bonds) and (6) correspond very closely in the range under consideration and for $N = 1, 2, 3$ the correspondence is exact. Two points are required to determine the two constants for both of these relations and in each case the curve determined by any two points passes through the third.

Parabolic equations of the type (6) fit the nitrogen–nitrogen (q,s = 1.330, 1.047) bond values[1] to within 0.14% and when used with the carbon–nitrogen (q,s = 1.582, 1.114) and phosphorus–phosphorus (q,s = 1.428, 1.816) single and triple bond values[1] lead to almost exactly the same predictions for the double bond values as do (1)[1] and Pauling's[6] covalent radii development. Thus, (1) and (8) fit the known experimental data equally well.

$$(1 - N/4)^2 = q(D - s) \qquad (8)$$

By a treatment based upon the molecular orbital method, Coulson[7] has calculated the bond-orders of benzene and graphite to be 1.667 and 1.53, respectively. Equation (6) leads to the values 1.670 and 1.522, while (1) yields the values 1.659 and 1.508 (D_{Benzene} = 1.39 Å., D_{Graphite} = 1.42 Å.).[1] These values agree closely with those derived by Coulson and evidently N of (1) and (6) may be interpreted as the bond-order as defined by Coulson's molecular orbital treatment.

Using the valence–bond resonance method, Penney[8] has calculated the values 1.623 and 1.45 for these same quantities. Taking the energy of the benzene bond to be $^1/_6\,(Q_f(\mathrm{Benzene})^5 - 6E_{\mathrm{C-H}}{}^6) = 85.9$ kcal. in (3) yields $N_{\mathrm{Benzene}} = 1.62$. However, since the interatomic distances appear to be more accurately determined than bond-energies, and E_{Benzene} is indirectly determined above, the former correspondence seems more significant.

Since this note was prepared for publication a paper by Bernstein[9] bearing upon this topic has appeared. By considerations of the form of equations (1) and (2) and a model for multiple carbon–carbon bonds Bernstein has been led to two essentially simplified equations of similar form which fit the known data remarkably well.

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RECEIVED MARCH 3, 1947

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[3] J. L. Kavanau, *J. Chem. Phys.*, **15**, 77 (1947).

[4] R. Cherton, *Bull. soc. chim. Belg.*, **52**, 26 (1943).

[5] The calculation of values to 4 digits is for comparative purposes.

[6] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940.

[7] C. A. Coulson, *Proc. Roy. Soc.* (*London*), **169A**, 413 (1939).

[8] W. G. Penney, *ibid.*, **158A**, 306 (1937).

[9] H. J. Bernstein, *J. Chem. Phys.*, **15**, 284 (1947). These equations are

$$D = D_1\left[\frac{2}{3} + \frac{1}{3}\left(\frac{n-1}{n+1}\right)^{\frac{N-1}{2}}\right]$$

for all symmetrical linkages, and

$$D = \left(\frac{Z - 1.50}{Z - 3.10}\right)\left[\frac{2}{3} + \frac{1}{3}\left(\frac{1}{3}\right)^{\frac{N-1}{2}}\right]$$

for symmetrical linkages of the first row atoms (Z = atomic number, D_1 = single bond distance). By using the additivity rule the bond distances for unsymmetrical links may be calculated.

The Solubility of Sodium Sulfamate in Water

BY STEPHEN H. LANING AND P. A. VAN DER MEULEN

Sodium sulfamate was first isolated and analyzed by Berglund[1] in 1878. Its solubility in water has been reported[2] to be 106 g. per 100 g. of water. Beck[3] reported its molal volume to be 53.7. No other data relating to the salt appear in the literature.

As we wished to use this compound in a study to be reported later we prepared and purified the salt and determined its solubility in water. The density and characteristic X-ray reflection data were also determined. The results of this work are reported below.

Experimental

Our salt was prepared by starting with ammonium sulfamate which had been purified by recrystallization four times from water. When dried the ammonium sulfamate had a melting point of 132.8°. A weighed quantity of this salt was treated with the calculated quantity of standard sodium hydroxide solution. The solution was evaporated under reduced pressure at a temperature of 40 to 45° to remove the ammonia and to concentrate the

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[1] E. Berglund, *Bull. soc. chim.*, [2] **29**, 422 (1878).

[2] M. E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

[3] G. Beck, *J. prakt. Chem.*, **156**, 227 (1940).

solution. When a solution nearly saturated at 45° is cooled to room temperature a voluminous crystalline hydrate separates. The removal of the crystals of this hydrate from the mother liquor by filtration is exceedingly difficult.

A crystalline precipitate which is less difficult to handle is obtained by the following procedure. A solution containing approximately 175 g. of sodium sulfamate in 100 g. of water is warmed to 55°, and methanol is added slowly until a slight permanent precipitate results. This solution is then allowed to cool to room temperature.

The crystals forming under these conditions are easily separated from the solution by filtration and can be washed with methanol. Crystals so produced were stored in a vacuum desiccator over phosphorus pentoxide. They are long transparent needles which show parallel extinction.

A weighed portion of the salt was converted to sodium sulfate and the sulfate was weighed. The per cent. of sodium found from this was 19.32 (calculated for the anhydrous salt 19.31%).

The density of the anhydrous salt at 20° was determined by means of a pycnometer, using carbon tetrachloride as the liquid. Two determinations showed the density to be 2.210 ± 0.002.

The powder was examined with a Norelco X-ray spectrometer. The wave length of the X-rays was 1.539 Å. produced from copper K-α radiation. Prominent lines of medium intensity were observed at the 2θ angles given in Table I.

TABLE I

ANHYDROUS SODIUM SULFAMATE X-RAY DIFFRACTION DATA

2θ Angle	Spacing, Å.	Intensity
9.25	9.55	Medium
21.20	4.18	Weak
22.75	3.90	Medium
24.40	3.65	Medium
27.60	3.25	Medium

Solubility Determination.—For the solubility determination we used a 25-ml. flask with two long necks. Through one of these was inserted a mechanical stirrer with a mercury seal, while the second served to withdraw samples. The flask was placed in a bath, held constant to ±0.10°. Samples were withdrawn at intervals of from one hour to two days by means of a pipet with a removable cotton plug on its tip. In all cases equilibrium was reached well within the time limit of two days. The samples of about three grams were placed in weighing bottles, weighed, and slowly evaporated under vacuum over phosphorus pentoxide in a desiccator. The bottles and contents were finally dried to constant weight at room temperature over phosphorus pentoxide.

The results are given in Table II.

TABLE II

SOLUBILITY OF SODIUM SULFAMATE IN WATER

Determinations	Temp., °C.	Solubility grams $NaSO_3NH_2$ per 100 grams water
5	0 (ice water)	79.90 ± 0.24
5	20	113.00 ± .16
5	30	135.93 ± .02
4	35	151.37 ± .02
4	40	168.56 ± .05
4	45	175.06 ± .02
5	50	182.17 ± .06
3	55	191.30 ± .03

Figure 1 constructed from these data shows that there is a sharp break in the solubility curve at 38.3° and a solubility of 165.2 g. of anhydrous salt in 100 g. of water.

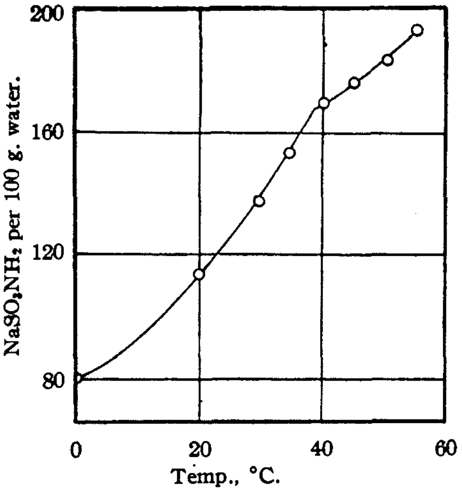

Fig 1.—Solubility of sodium sulfamate in water.

The composition of the crystals in equilibrium with the saturated solution below and above the transition point was determined by separate experiments.

Weighing bottles containing one gram of anhydrous salt or one gram of anhydrous salt and a specified quantity of water, were placed in desiccators containing certain saturated salt solutions and held at a temperature near 20°. In some of the desiccators the aqueous tension was such as to produce a gain in weight, in others to produce a loss in weight of the bottles and contents, as summarized in Table III.

TABLE III

HYDRATION OF SODIUM SULFAMATE

Sample no.	Initial g. water per g. $NaSO_3NH_2$	Saturated aqueous solution in desiccator	Vapor[a] pressure at 20°	Remarks
1	0.0	NH_4Cl	13.9	Continues to gain weight until solution results
2	.4856	$NaNO_3$	11.6	Lose weight till the monohydrate remains
3	.3217	$NH_4Cl + KNO_3$	12.7	
4	.0	$NaNO_3$	11.6	Gains weight till the monohydrate remains

[a] "International Critical Tables," Vol. I, p. 67.

As soon as the water content of Sample 1 exceeded that of the monohydrate, solution was formed and continued to be formed until the salt had dissolved completely. Samples 2, 3 and 4, came to constant weight when they contained 0.152 g. of water per gram of anhydrous salt. To form the monohydrate, one gram of anhydrous salt would combine with 0.1512 g. of water.

The composition of the solid phase above the transition point was determined by the well-known method[4] in which a third component not taken up by the solid phase is added to the solution. Sodium sulfamate, sodium chloride and water were brought together and warmed to about 90° at which temperature the solutions were homogeneous. Samples of these solutions were removed for analysis. The solutions were then cooled to about 45° and allowed to crystallize. Samples of the mother liquor were withdrawn and also analyzed. In all cases water was determined by evaporating to dryness and weighing the residue. Sodium chloride in the residue was determined by a Volhard titration. The results are given in Table IV.

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(4) A. Findlay, "The Phase Rule and Its Applications," 8th ed., Longmans, Green and Co., New York, N. Y., 1938, p. 272.

TABLE IV

COMPOSITION OF ORIGINAL SOLUTION AND OF MOTHER LIQUOR EQUILIBRIUM WITH SODIUM SULFAMATE

Expt.	Original solution % H_2O	Original solution % NaCl	Mother liquor % H_2O	Mother liquor % NaCl	% H_2O in the solid, by calculation
1	31.22	3.880	36.85	4.539	−1.93
2	34.64	2.814	37.14	3.026	+1.46
3	35.83	7.125	38.42	7.627	−1.00
4	28.23	3.745	37.60	5.033	+1.00
5	28.70	3.115	36.88	4.043	+1.23

The results clearly indicate that the solid phase above the transition point is the anhydrous salt.

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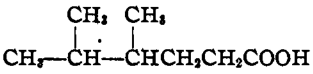
γ-Isopropyl and γ-Cyclohexyl Valeric Acids

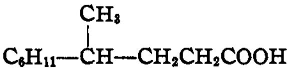
BY NATHAN LEVIN,[1] DOMENICK PAPA AND ERWIN SCHWENK

In connection with some experimental work in progress in these laboratories, it was necessary to prepare γ-isopropyl (I) and γ-cyclohexyl valeric acids (II).



$$CH_3-CH(CH_3)-CH(CH_3)CH_2CH_2COOH$$

(I)



$$C_6H_{11}-CH(CH_3)-CH_2CH_2COOH$$

(II)

The preparation of several γ-substituted alkanoic acid esters has been reported recently by Cason and co-workers.[2] According to the method of these workers, γ-substituted alkenoic acid esters, obtained from the corresponding γ,γ-disubstituted butyrolactones, were reduced catalytically to the corresponding saturated esters using platinum oxide catalyst. In our studies, attempts to reduce the ethyl ester of γ-isopropyl and γ-cyclohexyl pentenoic acids using platinum oxide catalyst failed completely. It was found, however, that these unsaturated acids, without further purification, could be reduced readily by nickel–aluminum alloy in alkaline solution according to the method used in these laboratories,[3] or catalytically, using Raney nickel. The presence of sulfur compounds apparently did not interfere with these reductions.

Experimental

γ-Methyl-γ-isopropylbutyrolactone.—This lactone was prepared essentially as described for the *n*-propyl analog.[2] A solution of isopropylmagnesium bromide in 500 cc. of ether was prepared in the usual manner from 72.9 g. (3.0 atoms) of magnesium and 230 cc. (2.45 moles) of isopropyl bromide. A portion of the solvent (200 cc.) was distilled off, the solution cooled, diluted with 300 cc. of anhydrous benzene and then added dropwise to a stirred solution of 317 g. (2.2 moles) of ethyl levulinate in 1.2 liters of benzene cooled to −5°. After decomposing the complex, the organic layer was separated, washed with water, 5% sodium bicarbonate solution, water, saturated sodium chloride solution and then dried over anhydrous sodium sulfate. The solvent was removed and the residue fractionated using an air-cooled Vigreux column 45 cm. in length. After a forerun of ethyl levulinate, the lactone distilled at 60–62° (1 mm.); yield 110 g. (35.1%).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.41; H, 10.29.

γ-Isopropylvaleric Acid (I).—Seventy and three-tenths grams (0.5 mole) of the above lactone and 99 cc. (1.5 moles) of thionyl chloride in 100 cc. of anhydrous benzene were refluxed on a steam-bath for three hours. The resulting solution was then added to a stirred solution of alcoholic hydrogen chloride at 0°. The solvents were removed and the residue heated under reflux at 185–190° for one and one-half hours and then distilled, b. p. 84–87° (10 mm.).

The crude unsaturated ester[4] was saponified by dissolving in 100 cc. of ethanol and refluxing with 200 cc. of 20% aqueous sodium hydroxide. After removing the ethanol, a solution of 60 g. of sodium hydroxide dissolved in 300 cc. of water was added, followed by the addition of 50 g. of nickel–aluminum alloy in the course of two to two and one-half hours. The saturated acid was isolated in the usual manner and distilled; b. p. 80–82° (1 mm.), $n^{24.5}$ 1.4315, yield 46 g. (64%).

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.19. Found: C, 66.79; H, 11.10.

The *p*-bromophenacyl ester melted at 56.0–57.5° after recrystallization from dilute alcohol.

Anal. Calcd. for $C_{16}H_{21}O_3Br$: C, 56.31; H, 6.20. Found: C, 56.42; H, 6.10.

γ-Methyl γ-Cyclohexylbutyrolactone.—A Grignard reagent was prepared from 31.1 g. (1.28 moles) of magnesium and 147.1 cc. (1.20 moles) of cyclohexyl bromide in 400 cc. of ether. The solvent (225 cc.) was removed, the mixture cooled, diluted with 300 cc. of anhydrous benzene and then added dropwise to a stirred solution of 144.1 g. (1.0 moles) of ethyl levulinate[5] in 750 cc. of benzene with cooling to −5°. The complex was then decomposed and the organic layer washed with water, 5% aqueous sodium carbonate, water and dried over anhydrous sodium sulfate. The residue remaining after removal of the solvent was fractionated. After a forerun of 30 g. of ethyl levulinate, there was obtained 70 g. (38.8%) of lactone, b. p. 120–122 (2 mm.), m. p. 55–56°. The yield of lactone was 48.5% based on ester consumed.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.61; H, 10.12.

Ethyl γ-Cyclohexylpentenoate.—A mixture of 109.4 g. (0.6 mole) of lactone and 131 cc. (1.8 moles) of thionyl chloride was refluxed on a steam-bath for three hours; the reaction mixture was then added to alcoholic hydrogen chloride; and, after removal of the solvents, the residue was heated for three hours at 195–200° and distilled. The yield of ester was 84 g. (66.6%), b. p. 91–93° (1 mm.), $n^{24.5}$ 1.4703.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.07; H, 10.50; sap. eq., 266.7. Found: C, 74.09; H, 9.99; sap. eq., 269.

γ-Cyclohexylpentenoic Acid.—The above ester (69.5 g., 0.33 mole) was refluxed for two hours with 40 g. (1.0

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[1] Present address: Burroughs-Wellcome & Company, Inc., Tuckahoe, New York.

[2] Cason, Adams, Bennett and Register, THIS JOURNAL, 66, 1764 (1944).

[3] Schwenk, Papa, Whitman and Ginsberg, *J. Org. Chem.*, 9, 175 (1944).

[4] A sample of the saponification mixture was condensed with *p*-bromophenacyl bromide and the crude ester after recrystallization from dilute alcohol gave colorless crystals, m. p. 72–73°. *Anal.* Calcd. for $C_{16}H_{19}O_3Br$: C, 56.65; H, 5.65. Found: C, 56.50; H, 5.88.

[5] In an attempt to improve the yield of the butyrolactone, butyl levulinate was used in place of the ethyl ester. However, the yield of lactone amounted to only 33% of theory with a considerable amount of the butyl levulinate being recovered.