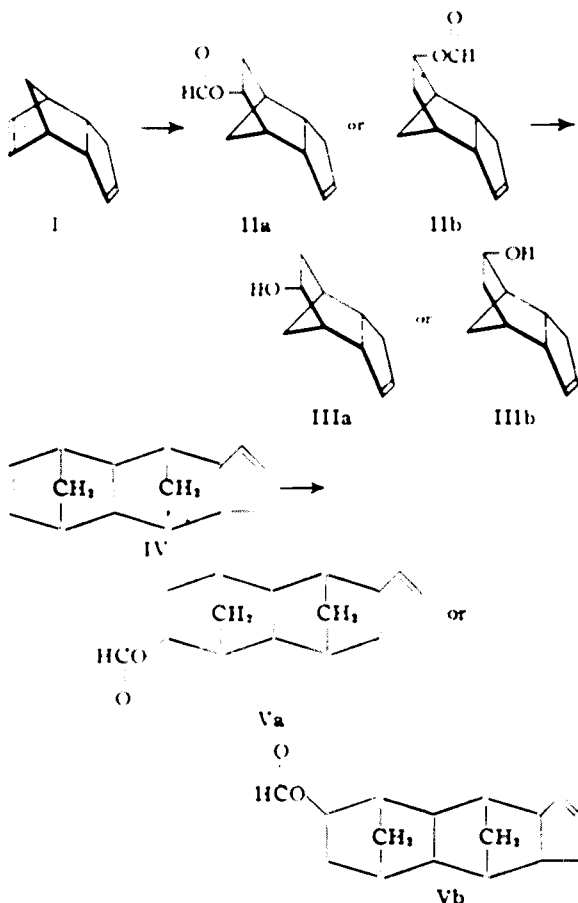


that even boiling formic acid ( $K_a^{25} = 1.77 \times 10^{-4}$ ;  $K_a^{100} = 1.55 \times 10^{-4}$ )<sup>6</sup> adds directly to I to produce dicyclopentenyl formate (IIa or b) in nearly quantitative yield, whereas Bruson states in his example that the addition of formic acid is achieved in about 71% yield by catalysis with 40% sulfuric acid. That our reaction likewise involves an "endo-exo-rearrangement," was shown by saponification of II to dicyclopentenol (IIIa or b), identical with the product obtained by direct hydration of I in the presence of sulfuric acid.<sup>3</sup>

The reaction described here provides a most convenient route for the preparation of dicyclopentenol and its higher homologs. We have found, *e. g.*, that tricyclopentadiene (IV) by the same method gives a quantitative yield of tricyclopentenyl formate (Va or b). In addition, we have been able to develop the uncatalyzed addition of formic acid into a method for the quantitative determination of dicyclopentadiene.<sup>7</sup>



#### Experimental

**Dicyclopentenyl Formate (II).**<sup>4</sup>—Crystalline dicyclopentadiene, m. p. 32° (132 g.; 1 mole), and formic acid, 99–100% (138 g.; 3 mole), were refluxed for four hours, and the mixture then fractionated. After removal of the excess formic acid, the formate II distilled at 136° (25

mm.). Yield was 171 g., 96%. Bruson<sup>3</sup> reports a boiling point of 111–112° (10 mm.):  $n_D^{20}$  1.4980;  $n_D^{15}$  1.5040;  $d_4^{15}$  1.113;  $M_R$  46.28.

*Anal.* Calcd. for  $C_{11}H_{14}O_2$ : C, 72.4; H, 7.9. Found: C, 74.3; H, 7.7.

The formate was saponified by refluxing with 1.5 equivalents of ethanolic potassium hydroxide for eight hours. The solvent was then distilled off, the residue taken up with benzene and washed with water. Dicyclopentenol (III) distilled at 92–95° (2 mm.), as a clear, colorless liquid of high viscosity. It exerts a strong anesthetic effect on the human tongue:  $n_D^{17}$  1.5206. Bruson<sup>3</sup> reports  $n_D^{20}$  1.5246. The phenylurethan of III melts at 163° (Bruson, 164–165°) and shows no depression upon admixture of the phenylurethan, prepared from dicyclopentenol according to literature.<sup>3</sup>

**Dihydro-dicyclopentenyl Formate.**—The formate (II) was mixed with an equal volume of 96% alcohol and hydrogenated over Raney nickel at room temperature and atmospheric pressure. The required amount of hydrogen was absorbed during two hours. Distillation gave a 92% yield of a colorless oil, b. p. 137° (35 mm.),  $n_D^{17}$  1.4870.

*Anal.* Calcd. for  $C_{11}H_{16}O_2$ : C, 73.3; H, 8.9. Found: C, 73.1; H, 9.0.

Tricyclopentenyl formate (V) was prepared in the same way, as described before, by eight hours of reflux. It boils at 136° (0.2 mm.) and forms a colorless, viscous liquid:  $n_D^{17}$  1.5352;  $d_4^{15}$  1.162  $M_R$  65.40; yield was quantitative.

*Anal.* Calcd. for  $C_{15}H_{20}O_2$ : C, 78.7; H, 8.2. Found: C, 78.6; H, 8.3.

Saponification of V, as described above, gave a 95% yield of tricyclopentenol in an excellent state of purity, b. p. 156° (0.4 mm.). The substance formed a hard, brittle glass, which after standing for three months crystallized spontaneously and then showed an m. p. of 115°, as described by Bruson and Riener.<sup>3</sup> No indication of the presence of an isomer was found.

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#### A Parabolic Relation between Bond-Order and Interatomic Distance

BY J. L. KAVANAU

The author<sup>1</sup> has advanced an empirical relation between bond-order,  $N$ , and interatomic distance,  $D$  (in Å.)

$$D = a + b \left( \frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N \quad (1)$$

where  $n_1$  and  $n_2$  are the principal quantum numbers of the valence electrons in the bonded atoms and  $a$  and  $b$  are constants for the specific atom pair.

Lagemann<sup>2</sup> has recently proposed a generalized modification of (1) to

$$D' = K_1/Z + K_2Z \left( \frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N \quad (2)$$

where  $Z$  is the sum of the atomic numbers of the bonded atoms and  $K_1$  and  $K_2$  are constant for all atom pairs having the same values for  $n_1$  and  $n_2$ . Lagemann has shown an average per cent. deviation of only 1.3% between experimental interatomic distance values and those given by equation (1) for a number of first row linkages.

(6) Harrod and Embree, *This Journal*, **96**, 1042 (1934)

(7) F. Bergmann and Japfe, *Ind. Eng. Chem., Anal. Ed.*, in press

(1) J. L. Kavanau, *J. Chem. Phys.*, **13**, 467 (1944)

(2) R. T. Lagemann, *ibid.*, **14**, 743 (1946)

The author<sup>1</sup> 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

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

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

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

where  $\gamma = 4 - 4\sqrt{1 - E/133}$ , relating  $E$  and  $D$  for carbon-carbon bonds. The numerical values<sup>1</sup> 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)<sup>1,2</sup> shows that the relation is very nearly linear. Cherton<sup>4</sup> has given a simple linear expression relating these variables. If we assume that this relationship is actually linear, then by setting

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

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<sup>5</sup>

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

and

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

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<sup>1</sup> 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<sup>1</sup> lead to almost exactly the same predictions for the double bond values as do (1)<sup>1</sup> and Pauling's<sup>6</sup> covalent radii development. Thus, (1) and (8) fit the known experimental data equally well.

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

By a treatment based upon the molecular orbital method, Coulson<sup>7</sup> has calculated the bond-orders of benzene and graphite to be 1.667 and

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

(4) R. Cherton, *Bull. soc. chim. Belg.*, **52**, 26 (1948).

(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).

1.53, respectively. Equation (6) leads to the values 1.670 and 1.522, while (1) yields the values 1.659 and 1.508 ( $D_{\text{Benzene}} = 1.39$  Å.,  $D_{\text{Graphite}} = 1.42$  Å.).<sup>1</sup> 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<sup>8</sup> has calculated the values 1.623 and 1.45 for these same quantities. Taking the energy of the benzene bond to be  $1/4 (Q_1(\text{Benzene})^2 - 6E_{\text{C-H}})$  = 85.9 kcal. in (3) yields  $N_{\text{Benzene}} = 1.62$ . However, since the interatomic distances appear to be more accurately determined than bond-energies, and  $E_{\text{Benzene}}$  is indirectly determined above, the former correspondence seems more significant.

Since this note was prepared for publication a paper by Bernstein<sup>9</sup> 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.

(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.

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LOS ANGELES 24, CALIFORNIA RECEIVED MARCH 3, 1947

## 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<sup>1</sup> in 1878. Its solubility in water has been reported<sup>2</sup> to be 106 g. per 100 g. of water. Beck<sup>3</sup> 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

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

(2) M. E. Cupery, *Ind. Eng. Chem.*, **20**, 627 (1938).

(3) G. Beck, *J. prakt. Chem.*, **186**, 227 (1940).