refrigerator. Within 24 hours a crystalline mass had formed in the flask. The supernatant liquid was decanted and the solid was recrystallized from methanol. The one gram of product (78.3 yield) was then sublimed at one mm. pressure for further purification, and this procedure gave a white crystalline product melting at 92.5–94°.

*Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.20; H, 7.26.

**Preparation of $\gamma$-Chloroisovaleronitrile.**—$\gamma$-Chloroisobutyl bromide was prepared according to Hearne, *et al.*[4]

Into a three-neck three-liter flask equipped with a gas-trapped reflux condenser, a mechanical stirrer, and a dropping funnel were placed 100 ml. of water and 103 g. (2 moles) of sodium cyanide. After solution of the cyanide, 700 ml. of 95% ethyl alcohol was added, followed by 305 g. (1.78 moles) of $\gamma$-chloroisobutyl bromide. The mixture was refluxed for two hours, cooled, and 600 ml. of water was added, followed by 200 ml. of chloroform. The layers were separated, and the chloroform layer was washed with an equal volume of water. After drying over calcium chloride, the chloroform was removed from the solution at atmospheric pressure, and the residue was fractionated at 15 mm. pressure. The fraction boiling at 79–83° and weighing 58 g. (27.7% yield) was collected. Cloke, *et al.*,[5] found the boiling point to be 82–83° at 16 mm.

**Condensation of $\gamma$-Chloroisovaleronitrile with Diphenylacetonitrile.**—The sodium salt of 19.3 g. (0.1 mole) of diphenylacetonitrile was prepared by refluxing 4.3 g. (0.11 mole) of sodamide with diphenylacetonitrile in 300 ml. of dry benzene for 90 minutes. The mixture was cooled, and 22 g. (0.2 mole) of $\gamma$-chloroisovaleronitrile was added dropwise with stirring. The resulting mixture was refluxed for 12 hours, cooled and poured into an equal volume of water. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. After removal of benzene under vacuum, the mixture was distilled until the vapor temperature reached 80° at 15 mm. Distillation at 2 mm. pressure gave as a first fraction diphenylacetonitrile, secondly an oil which was a mixture of diphenylacetonitrile and the product VI and a third fraction which was VII. The second fraction was cyclized as shown below.

**Cyclization to 2,2-Diphenyl-4-methyl-5-cyanocyclopentanone Imine.**—Into a three-neck 200-ml. flask equipped with a mechanical stirrer and a reflux condenser was placed 50 ml. of dry *t*-butyl alcohol and 0.2 g. of sodium metal. The mixture was refluxed until complete solution of the sodium occurred, and 8 g. of the second fraction from the preceding reaction, dissolved in 20 ml. of dry *t*-butyl alcohol, was added all at once. The mixture was refluxed for four hours, cooled and one ml. of water was added. The solution was evaporated to 50 ml., whereupon trituration with petroleum ether caused crystallization. After two recrystallizations from methanol, white crystals of 2,2-diphenyl-4-methyl-5-cyanocyclopentanone imine, melting at 133–135°, were obtained.

*Anal.* Calcd. for $C_{19}H_{18}N_2$: N, 10.22. Found: N, 10.12.

**Preparation of 4-Methyl-2,2-diphenylcyclopentanone from the Iminonitrile VII.**—A mixture of 2.3 g. of the iminonitrile (VII) 4.5 ml. of concd. sulfuric acid and 1.3 ml. of $H_2O$ was warmed on a steam-bath until the solid dissolved and the resulting solution was heated on the steam-bath for 20 minutes. The solution was cooled and a mixture of 20 ml. of water and 20 ml. of acetic acid was added. The resulting mixture was refluxed for 20 hours. It was then cooled and extracted with ether. The ether layer, after being washed with water and then with a solution of sodium bicarbonate, was dried over magnesium sulfate. After distillation of the solvent an oily residue remained. This was dissolved in petroleum ether and the solution was cooled with Dry Ice, the crystals which separated were recrystallized from a mixture of methanol and water and gave 1.4 g. (66.3%) of product which melted at 58.5–59.5°.

*Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.55; H, 7.33.

The 2,4-dinitrophenylhydrazone melted at 191–192° after being recrystallized from ethyl acetate.

*Anal.* Calcd. for $C_{24}H_{22}N_4O_4$: N, 13.03. Found: N, 13.10.

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[4] G. Hearne, Ervin Stehr, T. R. Steadman and L. C. Westcott, *Ind. Eng. Chem.*, **33**, 385 (1941).

[5] J. B. Cloke, Ervin Stehr, T. R. Steadman and L. C. Westcott, This Journal, **67**, 1587 (1945).

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## Dipole Moments and Structure of Acid Amides

By W. D. Kumler

In a recent paper Bates and Hobbs[1] imply that they were unable to calculate the dipole moment of acetamide from our data[2] because it scattered so widely. In Fig. 1 is a graph of the data showing that all three points fall near a straight line. The dipole moment of acetamide calculated from this line by the method of Halverstadt and Kumler[3] has a value of 3.92 *D* in good agreement with the value of 3.90 *D* reported by Bates and Hobbs.

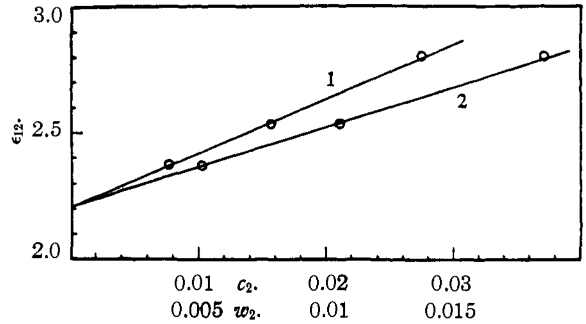

Fig. 1.—Plot of $\epsilon_{12}$ *vs.* $c_2$ (curve 1) for acetamide taken directly from Kumler and Porter's paper This Journal, **56**, 2549 (1934), and a plot of $\epsilon_{12}$ *vs.* $w_2$ (curve 2) for the same solutions.

These authors claim the usual polar resonance form makes a negligible contribution to the structure of amides because the theoretical moment of acetamide of 3.1 *D* which they calculate from the dimensions and angles obtained in the crystalline state, is near the gas value of 3.4–3.5 *D*.[4] This argument can have validity only if the molecule has the same configuration in the gas as it has in the crystal. No evidence has been given that this is the case. If it is assumed that the molecule does have the same configuration in the gas as in the crystal, it becomes pertinent to inquire how the molecule could be so held in the gas. The structure they have assumed is coplanar with one of the N–H dipoles pointing in nearly the same direction as the C=O dipole. This structure is opposed by both dipole or electrostatic forces and steric effects, since these would cause both amino hydrogens to be as close as possible to the oxygen atom and as far as possible from the methyl hydrogens. The absence of crystal forces leaves only resonance to account for the molecule having a planar configuration in the gas. Furthermore, the resonance must be of considerable magnitude to overcome both the dipole interaction and steric effects and, hence

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[1] W. W. Bates and M. E. Hobbs, This Journal, **73**, 2151 (1951).

[2] W. D. Kumler and C. W. Porter, *ibid.*, **56**, 2549 (1934).

[3] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[4] They do not state how this gas value was obtained, but presumably it is an estimate obtained by analogy with the known gas and solution values of formamide.

the polar resonance form must make an appreciable contribution to the over-all structure of the molecule.

Bates and Hobbs claim that the low basicity of the amide group is due mainly to dipole interaction. Since dipole interaction opposes a coplanar configuration, it is logical to conclude that if this effect is stronger than the resonance effect, the structure they have assumed for their calculations would not exist.

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## The Infrared Spectrum of Disulfur Decafluoride

BY D. EDELSON

Disulfur decafluoride, $S_2F_{10}$, is one of the fluorides of sulfur formed when sulfur is heated in a fluorine atmosphere; its properties have been described by Denbigh and Whytlaw-Gray.[1] It may be obtained as a by-product in the production of sulfur hexafluoride and is frequently present in the latter as impurity. In this work the infrared spectrum of this compound is reported as a means of comparing its structure to that of $SF_6$ of which it may be considered a dimer.

Measurements[2] were made on a double-beam spectrophotometer using a four-inch cell with potassium bromide windows. A sodium chloride prism was used to cover the range 2.5–15 μ, and a potassium bromide prism for 15–22 μ. The spectrum was measured at two pressures, 4 mm. and 37 mm. Results are shown in Fig. 1. The bands and their intensities are given in Table I.

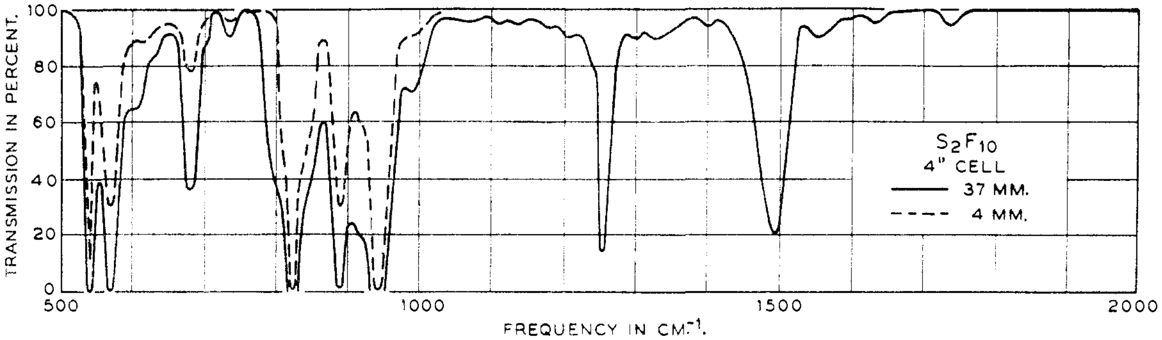

Fig. 1.—The infrared spectrum of $S_2F_{10}$.

TABLE I

INFRARED BANDS OF $S_2F_{10}$ (CM.$^{-1}$)

vs, very strong; s, strong; m, medium; w, weak; vw, very weak

| | | | |
|---|---|---|---|
| 544 | s | 1182 | w |
| 576 | s | 1206 | w |
| 605 | w | 1242 | m |
| 683 | m | 1256 | s |
| 733 | w | 1299 | w |
| 827 | vs | 1323 | w |
| 890 | s | 1404 | w |
| 917 | s | 1497 | s |
| 940 | vs | 1550 | w |
| 988 | m | 1629 | w |
| 1107 | vw | 1736 | w |
| 1130 | vw | | |

$S_2F_{10}$ may be assumed to consist of two half-octahedra of five fluorine atoms about a central sulfur atom, in analogy with the structure of $SF_6$, joined by a S–S bond. Although the fundamentals cannot be definitely assigned without further knowledge of the extent of rotation about the S–S bond,[3] and without the Raman spectrum, some tentative assignment may be made by a comparison with the spectrum of $SF_6$. The vibration of the plane of four fluorine atoms with respect to the central sulfur atom in $SF_6$ is given by the $F_{1u}$ fundamental[4] at 940 cm.$^{-1}$; the corresponding vibration in $S_2F_{10}$ may be assigned to the very strong band at 940 cm.$^{-1}$. This band in $S_2F_{10}$ is considerably stronger than that in $SF_6$, undoubtedly because there are twice as many vibrating groups per molecule.

It is questionable whether a S–S vibration should be expected to appear in the infrared; if this may be assumed, however, the bands at 544 or 576 cm.$^{-1}$ may be attributed to this in comparison with the value 512 cm.$^{-1}$ reported by Venkateswaran[5] for this frequency in $S_2Cl_2$.

The assistance of Mr. K. H. Storks and Mrs. M. H. Read in the experimental work is gratefully acknowledged.

[1] K. G. Denbigh and R. Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934).

[2] The sample used in these experiments was obtained through the courtesy of the Pennsylvania Salt Mfg. Co., Chestnut Hill, Phila., Pa.

[3] NOTE ADDED IN PROOF: S. H. Bauer, in a paper presented at the 120th meeting of the American Chemical Society at New York, September 6, 1951, Symposium on Bond Strengths, reported the existence of some hindered rotation despite an abnormally long S–S bond distance.

[4] R. T. Lagemann and E. A. Jones, *J. Chem. Phys.*, **19**, 534 (1951).

[5] S. Venkateswaran, *Ind. J. Phys.*, **6**, 275 (1931).

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## Silicon Disulfide and Silicon Diselenide[1a]

BY HENRY GABRIEL[1b] AND C. ALVAREZ-TOSTADO

The fact that silicon and the sulfur family elements react to form binary compounds has been known since the discovery of these elements and

[1a] Extract from a dissertation prepared under the direction of Prof. Alvarez-Tostado and submitted to the Dept. of Chemistry of Stanford University by Henry Gabriel in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

[1b] Fisk University, Nashville, Tenn.