

cases since ring closure is to a position meta to a methoxy group.^{19a}

The monomolecular cyclization of ζ -phenylenanthic acid would produce benzocyclononanone, a ring system which could not be found in the literature. Polyphosphoric acid converted the enanthic acid to a nearly colorless solid, insoluble in most solvents. The solid exhibited no tendency toward distillation at 280° (0.01 mm.) in a micro-sublimation apparatus with a cold finger condenser and was abandoned as polymeric.

The polyphosphoric acid cyclization of δ -3,4,5-trimethoxyphenylvaleric acid was distinguished by the fact that colorless crystals could be obtained in quantitative yield simply by diluting with water and cooling after the heating period in polyphosphoric acid was over.

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Experimental²⁰

3,4,5-Trimethoxycinnamylidenemalonic Acid.—The following illustrates the procedure used on all of the aldehydes in Table I. **Method A:** 3,4,5-Trimethoxybenzaldehyde, purified by means of the bisulfite compound followed by recrystallization from cyclohexane or from petroleum ether (60–70°) (4.9 g., 0.025 mole) melting at 74–76° was added to 14 cc. of ethyl ethylidenemalonate^{21,22} and 35 cc. of absolute ethyl alcohol. After swirling to dissolve as much as possible of the aldehyde, 10 g. of potassium hydroxide pellets was added and the stoppered flask was swirled under the tap so that room temperature was maintained. Solid separated usually before the last of the alkali had dissolved. The reaction was then set aside for 24–48 hours at room temperature. The mixture was then cooled in ice-water and acidified by the addition of a cold solution of 20 cc. of concentrated hydrochloric acid in 140 cc. of water. After standing overnight at 5°, the yellow crystals were filtered and washed with cold water. The product was then dried in air or in a vacuum desiccator overnight. **Method B:** 3,4,5-Trimethoxybenzaldehyde (0.025 mole) was combined with 9.3 cc. of ethylidenemalonic ester as above and treated with 55 cc. of 35% methanolic benzyltrimethylammonium hydroxide. An equivalent amount (26 cc. per 0.025 mole of aldehyde) of 50% methanolic choline was substituted for benzyltrimethylammonium hydroxide in two experiments. In all cases only a slight amount of heat was noted on mixing. After standing as above, a clear dark red solution was obtained. The ester was saponified by the addition of 120 cc. of water and refluxing for 30–60 minutes. After cooling, 40 cc. of 1:1 hydrochloric acid was added and the precipitated crystals were cooled at 5° overnight. The product was dried as before.

The cinnamylidenemalonic acids were purified by recrystallization from methanol. Recrystallization by dissolving in a small amount of warm ethanol, addition of benzene and distillation to remove the alcohol gave excellent recoveries and was superior to methanol where the crude products contained oil.

γ -Phenylpropylmalonic Acids.—The above acids were dissolved or suspended in absolute ethyl alcohol and shaken

(19a) Numerous examples of the decreased yield in cyclization to a position meta to a methoxy group have been collected. W. S. Johnson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 120.

(20) Melting points are uncorrected.

(21) F. R. Goss, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **123**, 3342 (1923). Ethyl ethylidenemalonate can be prepared in 86% yield in a hydrogenation bomb provided that the entire reaction mixture is distilled at 20 mm.

(22) I. Vogel, *ibid.*, **130**, 1985 (1927).

with 0.5–5.0% platinum oxide under hydrogen at a pressure slightly above atmospheric. Reduction proceeded rapidly and indicated the presence of two double bonds (Table I).

δ -Phenylvaleric Acids.—The colorless malonic acids were heated at 18 mm. in a large test-tube immersed in an oil-bath. Gas was evolved at 170–180° and the reaction was complete in 15 minutes.

Benzosuberones.—The method used was that reported,⁶ using 6.0 g. of polyphosphoric acid per 0.001 mole of the valeric acid and a 30-minute heating period at 95°.

δ -2-Methoxyphenyl-, δ -4-methoxyphenylvaleric acids and ζ -phenylenanthic acid gave high melting neutral compounds insoluble in the common solvents and not distillable at low pressures. These are probably the products of intermolecular condensation. Cyclization of the acid chlorides of the first two with aluminum chloride in nitrobenzene (room temperature overnight) gave only the starting acid.

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A Reinvestigation of the Structure of Difluoromethane by Electron Diffraction

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An early electron-diffraction investigation¹ of the structure of difluoromethane led to the parameter values $C-F = 1.36 \pm 0.02 \text{ \AA.}$, $\angle F-C-F = 110 \pm 1^\circ$, $C-H = 1.06 \text{ \AA.}$ (assumed) and $\angle H-C-H = 109^\circ 28'$ (assumed). Recently, an analysis of the infrared spectrum² of this substance, based upon the approximate symmetric top character of the molecule, led to two rotational constants and the parameter values $C-F = 1.32 \pm 0.01 \text{ \AA.}$, $\angle F-C-F = 107.0 \pm 0.5^\circ$, $C-H = 1.094 \text{ \AA.}$ (assumed) and $\angle H-C-H = 110^\circ$ (assumed). Because of the serious discrepancies between the results of these two methods for the principal parameters (which cannot, of course, be explained by the difference between the assumed values for the remaining parameters), it seemed that a reinvestigation of the structure was in order.

The sample of difluoromethane, supplied by the Jackson Laboratory of the du Pont Co., contained 0.2–0.3% fluoroform and 0.05% chlorodifluoromethane. The camera distance was 10.91 cm. and the electron wave length 0.06056 Å. The methods used in the structure determination have been described elsewhere.³

Theoretical intensity curves were calculated over the shape parameter range $C-F/F \cdots F = 1.36/2.14$ to $1.36/2.23$, assuming $C-H/C-F = 1.09/1.36$ and $\angle H-C-H = 109^\circ 28'$. All terms except $H \cdots H$ were included, and in the factor $\exp(-a_{ij}q^2)$, a was given the values 0.00016 and 0.00030 for the $C-H$ and $H \cdots F$ distance, respectively, in accord with our experience, and zero elsewhere.⁴

It is our conclusion that the best agreement with the appearance of the photographs is given by a curve slightly closer to J than I (Fig. 1). The factors of particular importance for this decision are the characters of the doubled maxima 3–4,

(1) L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

(2) H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 640 (1949).

(3) K. Hedberg and A. J. Stosick, *THIS JOURNAL*, **74**, 954 (1952).

(4) Some curves were calculated using values of $a_{F \cdots F}$ different from zero, however. It was concluded that $a_{F \cdots F}$ might be as large as about 0.00005 relative to $a_{C-F} = 0$, but that use of the value zero caused no error in the values of determined parameters.

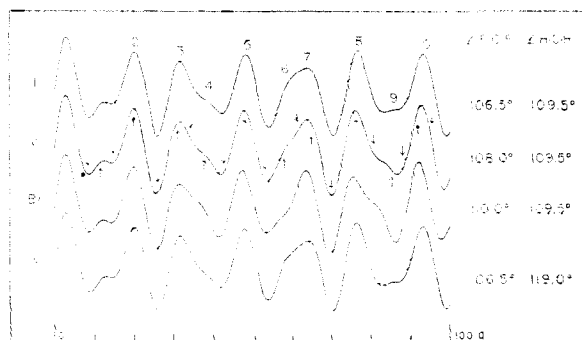


Fig. 1.—Difluoromethane: theoretical intensity curves.

and 6-7, the position of maximum 9, and the relative depths of minima, 5, 6 and 8. Such qualitative considerations and comparisons of the observed and calculated positions of maxima and minima (see Table I for an example close to our final model) lead to the following values of the structural parameters: C-F/C-H = 1.36/1.09 (assumed), C-F = 1.357 ± 0.017 Å., \angle F-C-F = $107.5 \pm 1.5^\circ$, \angle H-C-H = 109.5° (assumed), symmetry C_{2v} (assumed). The effect of varying the H-C-H angle is small (compare curves I and L), and any possible error in the assumed value can have no significant effect upon the values of the determined parameters.

TABLE I

COMPARISONS OF OBSERVED AND CALCULATED POSITIONS
Maxima and Minima (Curve J)

No.	Minima		Maxima	
	$Q_{\text{obsd.}}^a$	$Q_{\text{calcd.}}/Q_{\text{obsd.}}$	$Q_{\text{obsd.}}$	$Q_{\text{calcd.}}/Q_{\text{obsd.}}$
1	8.15	(1.067)	11.17	(1.083)
2	15.09	(0.928)	19.95	(0.995)
3	25.94	0.991*	31.02	1.017
4	34.26	1.036	37.69	1.008
5	42.67	0.980	47.84	0.997*
6	52.67	1.020	57.71	1.005
7	61.35	0.978	64.96	0.978
8	70.09	0.999*	76.19	.998*
9	80.46	1.007	85.05	.976
10	87.95	0.984	91.30	1.014
11	95.04	1.036		
Average 17 features		0.9990		
Average deviation		0.014		
Average 4 starred features		0.9963		
Average deviation		0.003		

Best model: C-F = $0.9980 \times 1.36 = 1.357$

^a Average of W. H. and K.H. measurements.

Our results differ significantly from those of the early electron diffraction study in the value of the F-C-F angle, which we find to be more than 2° smaller. Our photographs, extending to a considerably larger scattering angle, presumably allow a more reliable interpretation of the difficult doublets 3-4 and 6-7 upon which the early angle determination was largely based as well as enabling us to see maximum 9, of which the position and degree of association with adjacent maxima are very F-C-F-angle sensitive. The C-F bond length result from the infrared investigation stands well outside our limit of error. It is to be noted, however,

that the preliminary results of a recent microwave investigation³ (which appeared during the course of our work) C-F = 1.36 Å., C-H = 1.09 Å., \angle F-C-F = 108° , \angle H-C-H = 112° , agree well with ours.

Acknowledgment.—We wish to thank Professor Verner Schomaker for his helpful comments regarding the interpretation of some of the more difficult features of the pattern.

(5) D. R. Lide, Jr., *Bull. Am. Phys. Soc.*, **27**, 51 (1952).

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The Heat of Combustion of Neodymium¹

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Introduction.—Only in recent years have some of the rare earth metals become available in highly purified form. The information available in the literature on the heats of formation of the rare earth oxides is in some cases very meager and in those cases where considerable data are available the agreement between the different investigators is poor. It was therefore thought desirable to make an investigation of the heats of formation of those rare earth oxides for which the metals could be obtained.

This paper reports the results obtained on neodymium metal. The only previous work found by us in the literature on the heat of formation of Nd_2O_3 is that of Muthmann and Weiss² who obtained $\Delta H_f = -435$ kcal./mole.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in an oxygen bomb calorimeter at 25 atmospheres pressure. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid and also was determined electrically. The completeness of combustion was determined by treating the combustion products with 6 *N* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the corresponding standard deviations.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.³ The energy equivalent of the calorimeter was $10,096.6 \pm 3.1$ joules/°.

Neodymium Metal.—The neodymium metal was supplied by Dr. F. H. Spedding of the Ames Laboratory of the Atomic Energy Commission. This metal was analyzed with the following results: Na, 0.02; Mg, 0.01; C, 0.034; N, 0.06; and O, 0.21. Any other metallic impurities were present in amounts too small to be detected by the spectroscopic method used. An X-ray Debye pattern of the metal showed only lines for the metal. There was no evidence of neodymium hydride.

Combustion of Neodymium.—The neodymium was burned as chunks on sintered discs of 99% pure Nd_2O_3 supported on a platinum platform weighing 103.8 g. A new disc was used for each run. Pure magnesium wire was used. Its heat of combustion was taken as 24,667 joules/g.³ The amount varied from 0.0087 to 0.0091 g. Correction was made for the electrical energy used in igniting the wire. The total energy equivalent of the calorimeter and contents was used, taking into account the disc, the platinum and the difference in energy equivalent between the neodymium

(1) This work was done under the auspices of the A.E.C.

(2) W. Muthmann and L. Weiss, *Ann.*, **331**, 1 (1904).

(3) C. E. Holley, Jr., and E. J. Huber, Jr., *This Journal*, **73**, 5577 (1951).