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The Structure and Infrared Absorption Spectra of Polynitrophenylmethylnitramines and Polynitroanilines[1]

BY W. C. LOTHROP, G. R. HANDRICK AND R. M. HAINER

The infrared spectra of six polynitro aromatic amines have been determined and found to support chemical evidence that so-called pentanitrophenylmethylnitramine (I) is in reality a tetranitrophenylmethylnitramine (III or IV). The structure of pentanitroaniline has been confirmed by infrared study. Major improvements are reported in the synthesis of 3,5-dinitroaniline and 3,5-dinitrodimethylaniline.

While investigating a theory relating performance of pure explosive molecules to their chemical structures,[2] anomalies were encountered with a compound described by Blanksma[3] as pentanitrophenylmethylnitramine (I), which he obtained by nitration of a crude sample of 3,5-dinitrodimethylaniline. This structure had been assigned on the basis of nitrogen analysis alone.

Repetition of the preparation of this substance by treating pure 3,5-dinitrodimethylaniline with 100% nitric acid gave a compound of the same melting point which was tested for explosive power in the Trauzl lead block and ballistic mortar, and was measured for heat of combustion. The power values were then compared with those predicted from calculated oxygen balance for pentanitrophenylmethylnitramine[2] and found to be much lower than expected. Similarly the observed heat of combustion was significantly higher than the value calculated according to the method of Kharasch.[4]

On this basis it seemed possible that an incorrect formula had been assumed for so-called pentanitrophenylmethylnitramine. Elementary analyses were therefore obtained, which showed that Blanksma's single nitrogen analysis was inadequate and that the compound in reality contained one less nitro group than postulated.

Since the compound could be a *tetra*nitrophenylmethylnitramine, the power, oxygen balance and heat of combustion values were re-estimated. As shown in Table I, these values agree closely with the observed values.

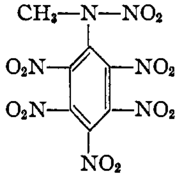
TABLE I

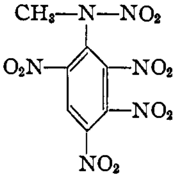
PHYSICAL PROPERTIES

			Penta-nitro-phenyl-methyl-nitra-mine calcd.	Tetranitrophenyl-methylnitramine	
		Un-known ob-served		Calcd.	Ob-served for 2,3,4,6-isomer
Power, % TNT	in Trauzl test[a]	151	166	152	157
	in ballistic mortar[b]	134	148	138	141
Q_c, cal./g.[c]		2453[d]	2040[e]	2431[e]	2510[d]
Oxygen balance		....	−14.9	−28.9	....
M.p., °C.		132 dec.	....	....	145 dec.

[a] Determined at National Fireworks, Inc., West Hanover, Mass. [b] Determined at Bureau of Mines, Bruceton, Pa. [c] Constant volume, H_2O liquid. [d] Determined at Picatinny Arsenal, Dover, N. J. [e] Calculated according to Kharasch[4] based on the additive value for aromatic $-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{N}}}-\mathrm{NO_2}$ derived from heat of combustion observed for tetryl and included in his data.

From its method of preparation and its composition, Blanksma's product could be expected to be one of the isomeric compounds II-V. Compound II has been prepared[3,5,6,7] and is different (see Table I). Compound V can be eliminated because the infrared absorption shows the presence of a nitramine group. This leaves III and IV as the possible structures of Blanksma's so-called pentanitrophenylmethylnitramine and it is not yet possible to distinguish between these structures.


I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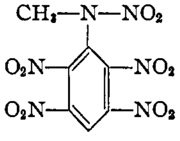
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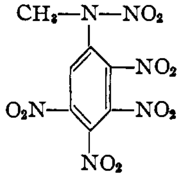
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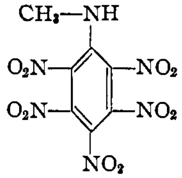
V

Evidence against the presence of the N-H or NH_2 groups and hence against structure V or any polynitro aniline was obtained by comparing the infrared absorption spectrum of the unknown with the spectra of several related compounds in the region 3200–3500 cm.$^{-1}$. The primary amines shown in Fig. 1, tetranitroaniline (1-E), picramide (1-F) and aniline (1-G), all exhibit double band absorption ascribable to the $-NH_2$ group in this region. N-Methylaniline (1-H), a secondary amine has broad but unique characteristic absorption in this region. On the other hand 2,3,4,6-tetranitrophenylmethylnitramine (1-C), tetryl (1-D), N,N-dimethylaniline (1-I) and the unknown (1-B) do not show such absorption.

That the unknown is a penta-substituted aromatic compound and has an aromatic -CH group is further implied by its absorption in the range of 3000 to 3150 cm.$^{-1}$. The compounds whose spectra are given in Fig. 1 and which are known to have one or more CH groups (1-C, 1-D, 1-E, 1-F, 1-G, 1-H and 1-I) show appreciable to marked absorption in this region. The intensity of absorption

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(1) This article is taken from work done under Contract W-19-020-ORD-6436 with the Office of the Chief of Ordnance and has been approved for publication by the Public Information Division, National Military Establishment.

(2) W. C. Lothrop and G. R. Handrick, *Chem. Revs.*, **44**, 419 (1949).

(3) J. J. Blanksma, *Rec. trav. chim.*, **21**, 265 (1902).

(4) M. S. Kharasch, *J. Research Nat. Bur. Standards*, **2**, 359 (1929).

(5) M. P. Van Romburgh, *Rec. trav. chim.*, **8**, 273 (1889).

(6) A. Forster and W. Coulson, *J. Chem. Soc.*, **121**, 1988 (1922).

(7) A. Stettbacher, *Tech.-Ind. Schweiz. Chem.-Ztg.*, **26**, 181 (1943); *C. A.*, **38**, 3128 (1944).

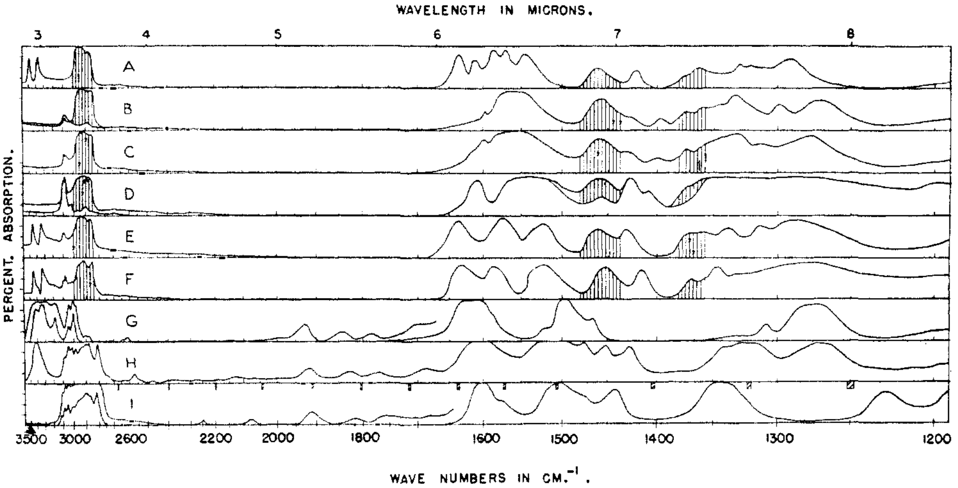

Fig. 1.—Infrared absorption spectra: calcium fluoride prism.

of the unknown (1-B) agrees with that of 1-C and 1-E each of which has but one aromatic –CH group; this is consistent with structures III and IV.

A rigid assignment of structure is not possible at this time. Some work of Macciotta[8] on the nitration of nitroanilines with mixed nitric and sulfuric acids, indicating that ortho positions are more readily filled than para positions, makes the 2,3,5,6-isomer (III) a reasonable choice. Our preparation, however, was made with nitric acid alone and may not follow the same course as nitrations with mixed acids. On the other hand, some recent observations concerning steric hindrance and the effects of substituents on the ortho–para ratio in aromatic substitution[9] would imply that the 2,3,4,5-isomer (IV) is the preferred product.

A compound believed to be pentanitroaniline was also studied, and the structure assigned by Flurscheim and Holmes from chemical evidence[10] was confirmed by observation of infrared spectra. The double band absorption at 3380 and 3400 cm.$^{-1}$, Fig. 1-A, is consistent with a primary amine structure while the absence of aromatic –CH groups is confirmed by the lack of absorption between 3000 and 3150 cm.$^{-1}$. Moreover, for pentanitroaniline, a structure having a calculated oxygen balance of -15%, the Trauzl lead block value found (163% TNT) is in harmony with prediction (165% TNT).[2]

A discussion of the infrared spectra may now be in order. Many of the nine compounds measured contain unusual multiplicity of nitro group substitution. The features in common which are most readily identified with molecular groups, *i.e.*, –NH, –NH_2, aromatic –CH, have already been discussed, but assignments of other absorption bands to certain molecular groups may also be made. All the primary amines absorb from 1630–1650 cm.$^{-1}$ (see Fig. 1-A, 1-E, 1-F and 1-G) while di- or trisubstituted amines do not absorb strongly in this region (see Fig. 1-B, 1-C, 1-D, 1-H and 1-I). Similar observations were made above for the 3500 cm.$^{-1}$ region.

The nitro compounds absorb in the region characteristic for the nitro group in other materials, *viz.*, 1500–1600 cm.$^{-1}$ and near 1300 cm.$^{-1}$. An unexpected feature is the absence in general of the aromatic ring absorption usually observed near 1500 and near 1600 cm.$^{-1}$. This may be due to the overlapping absorption of stronger bands or to modification of the absorption due to the high degree of substitution. It is also interesting to note the very considerable difference in spectra of the isomeric tetranitrophenylmethylnitramines, particularly below 1300 cm.$^{-1}$. This is an excellent indication of the effect on the infrared absorption of shifting a nitro group from the 4- or 6-position (Fig. 1-C) to the 5-position (Fig. 1-B).

The data found in Fig. 2 are considered to be in the region characteristic of the individual compounds and are not interpretable in terms of individual structural features.

Acknowledgment.—We are indebted to Dr. T. L. Grave (Evans Research and Development Corp., New York City, N. Y.) and to Dr. E. R. Atkinson (University of New Hampshire, Durham, N. H.) for preparing most of the compounds listed.

Experimental

The compounds used in the infrared measurements are listed in Table II with their melting or boiling points and source of supply. Those obtained from commercial sources were used as received without purification. The methods of synthesis for the others are briefly described below. Preparation of tetranitrophenylmethylnitramine (III or IV), 3,5-dinitroaniline and 3,5-dinitrodimethylaniline are given in considerable detail because of certain new or improved features of synthesis.

Infrared Experimental Techniques.—The data shown in Figs. 1 and 2 were obtained on a modified Perkin–Elmer infrared spectrometer and are direct tracings of experimental data in per cent. absorption *vs.* frequency in wave numbers (cm.$^{-1}$). Spectra shown in Fig. 1 were obtained using a calcium fluoride prism and the results have been idealized to eliminate absorption due to atmospheric water vapor and carbon dioxide. Spectra shown in Fig. 2 were obtained using a sodium chloride prism and contain minor absorption due to atmospheric water vapor at 1600 ± 200 cm.$^{-1}$ and due to carbon dioxide at 670 cm.$^{-1}$.

The spectra for all the solid compounds were obtained from crystals triturated in mineral oil and observed in such sample thickness (approximately 0.001 inch) as to obtain adequate absorption. The absorption attributed to mineral oil is indicated on the reported spectra by cross-hatching.

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[8] E. Macciotta, *Gazz. chim. ital.*, **71**, 81 (1941).

[9] P. B. D. de la Mare, *J. Chem. Soc.*, 2871 (1949).

[10] B. Flurscheim and E. L. Holmes, *ibid.*, 3041 (1928).

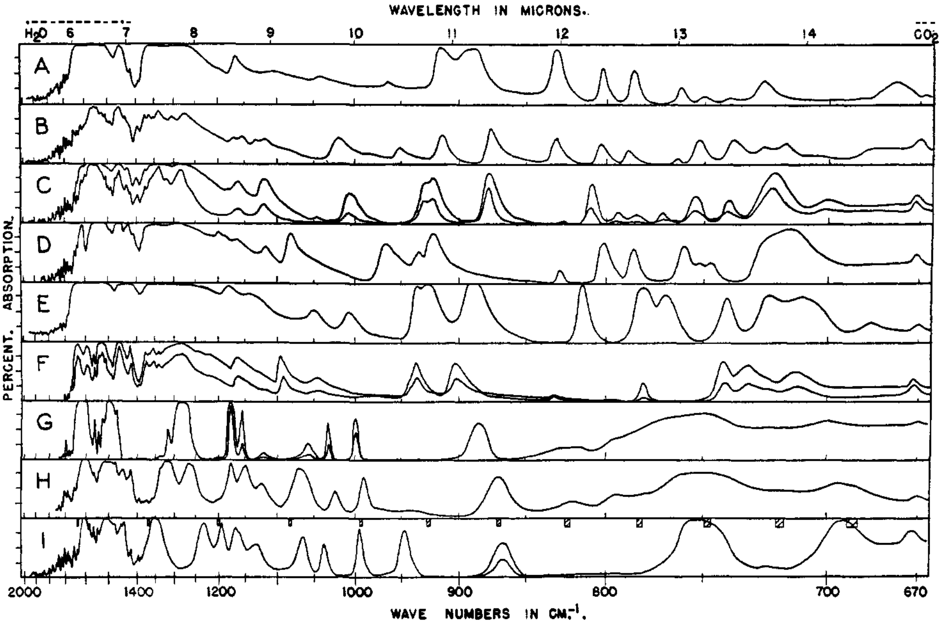

Fig. 2.—Infrared absorption spectra: sodium chloride prism: A, pentanitroaniline; B, 2,3,4,5- or 2,3,5,6-tetranitrophenylmethylnitramine; C, 2,3,4,6-tetranitrophenylmethylnitramine; D, 2,3,6-trinitrophenylmethylnitramine; E, 2,3,4,6-tetranitroaniline; F, picramide; G, aniline; H, N-methylaniline; I, N,N-dimethylaniline.

TABLE II

DATA FOR INFRARED SPECIMENS

Name	M.p., °C. Obsd.	Lit.	Source	Spectrum Figs. 1 and 2
Pentanitroaniline	196–198 dec.	192 dec.[10]	Synthesis	A
Tetranitrophenylmethylnitramine (2,3,4,5- or 2,3,5,6-isomer)	131–132 dec.	132[3]	Synthesis	B
2,3,4,6-Tetranitrophenylmethylnitramine (Nitrotetryl)	146–147 dec.	145[3]	Synthesis	C
Tetryl (2,3,6-trinitrophenylmethylnitramine)	129–130	...	Picatinny Arsenal	D
2,3,4,6-Tetranitroaniline	215–218 dec.	216–217[16]	Synthesis	E
Picramide	189–192	188[17]	Synthesis	F
Aniline	b. 183–186	...	Baker C.P.	G
N-Methylaniline	b. 81–82 (14 mm.)	...	Eastman	H
N,N-Dimethylaniline	1.5–2.5	...	Eastman	I

To elucidate further the absorption in the 3μ region pentanitroaniline (1-A), tetranitrophenylmethylnitramine (1-B) and tetryl (1-D) were observed in perfluorokerosene which does not absorb in this region. In addition, the spectrum of tetryl was corrected by this means between 1350 and 1500 cm.$^{-1}$. The liquid amines were measured in the pure state.

Pentanitroaniline was prepared by nitrating 3,5-dinitroaniline with mixed acid in the manner described by Flurscheim and Holmes.[10] A small amount of lead sulfate was found to catalyze the rearrangement of the intermediate primary nitramine to pentanitroaniline.

Because the preparation of **3,5-dinitroaniline** by the method of Flurscheim,[11] by reduction of trinitrobenzene with ammonium hydrosulfide, has several disadvantages, an improved synthesis from 3,5-dinitrobenzoic acid was accomplished using the Schmidt reaction.[12] A solution of 100 g. (0.47 mole) of 3,5-dinitrobenzoic acid in 180 ml. of 20% oleum and 40 ml. of concentrated sulfuric acid was prepared in a 2-liter, 3-neck flask equipped with reflux condenser, thermometer, dropping funnel and mechanical stirrer. Chloroform (300 ml.) was added and the temperature was raised to 45°. With rapid stirring 35 g. (0.54 mole of powdered sodium azide was added in small portions, maintaining the temperature at 35–45°. Reaction was accompanied by foaming, and no more than 5 g. was added at the start until nuclei of white foam had appeared. After all the sodium azide had been added, the temperature was raised until the chloroform refluxed vigorously, where it was held for three hours. The reaction mixture was cooled, poured onto 1 kg. of ice, and six liters of cold water was added. After standing for at least one hour, the fine yellow precipitate was separated by filtration, washed thoroughly with water and dried. The yield was 78 g. (90%) of 3,5-dinitroaniline melting at 162–163°.

Although **3,5-dinitrodimethylaniline** was prepared by Blanksma[3] from dinitroaniline and dimethyl sulfate and used in a crude form, the pure compound has been described in the literature only recently.[13] Roberts and Selby converted 3,5-dinitroaniline hydrobromide to dimethyldinitroaniline (m.p. 164°) in 65% yield by heating at 100° with methanol in a sealed tube. In our hands the more convenient reductive alkylation method of Clarke, *et al.*,[14] was found to give higher yields of pure 3,5-dinitrodimethylaniline. 3,5-Dinitroaniline (60 g., 0.33 mole) was dissolved in 1200 ml. of distilled, commercial formic acid by heating at 85°. Formaldehyde (100 ml. of 37% solution) was added and the heating continued on a steam-bath for two hours while an additional 260 ml. of formaldehyde was added. The solution was then refluxed for two hours and allowed to cool overnight. The orange crystals which separated were collected by filtration, washed thoroughly with water, and dried. The yield of 3,5-dinitrodimethylaniline was 62 g. (90%); m.p. 164–165°. No additional product was obtained by concentrating the mother liquors.

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[11] B. Flurscheim, *J. prakt. Chem.*, **71**, 537 (1905).

[12] H. Wolff, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 307.

[13] J. C. Roberts and K. Selby, *J. Chem. Soc.*, 2785 (1949).

[14] H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

Tetranitrophenylmethylnitramine was synthesized using pure dinitrodimethylaniline. To a flask containing 500 ml. of nitric acid (d. 1.52; distilled from dry potassium nitrate and sulfuric acid) cooled to −5° was added 40 g. (0.19 mole) of 3,5-dinitrodimethylaniline during the course of 45 min. The temperature was kept below 0° during the addition. The nitration mixture was allowed to come gradually to room temperature and then to stand for at least 16 hr. The nitric acid solution was again cooled to 0° while approximately 200 ml. of ice-cold distilled water was added. The nitramine, which precipitated as a finely-crystalline light buff-yellow powder, was separated by filtration, dried and recrystallized from dry, warm ethylene dichloride. The yield of product melting at 131–132° (dec.) was 31.5 g. (50%). *Anal.* Calcd. for $C_7H_4N_6O_{10}$: C, 25.31; H, 1.21; N, 25.31. Found: C, 25.50, 25.42, 25.42; H, 1.41, 1.38, 1.35; N, 25.49. Found by Blanksma[8]: N, 25.8.

2,3,4,6-Tetranitrophenylmethylnitramine was obtained in the manner of Blanksma[8] from *m*-nitroaniline by methylation followed by nitration. In a typical experiment 28 g. (0.2 mole) of *m*-nitroaniline was added slowly to a stirred suspension of 88 g. (0.7 mole) of dimethyl sulfate in 125 ml. of water. During the addition and subsequent stirring at room temperature (reaction time 2 hr.) solid soda ash was added as necessary to keep the solution basic to phenolphthalein. At the conclusion of the reaction, the mixture was heated to 50° and additional alkali added to destroy excess dimethyl sulfate.

The dark red solid which appeared upon cooling was filtered, and purified by steam distillation to separate it from a small amount of non-volatile material. About 3 l. of distillate was collected, from which was obtained 15 g. (45%) of *m*-nitromethylaniline melting at 51–59°.

Attempted N-methylation of *m*-nitroaniline by the method of Clarke[14] which had been successful with dinitroaniline gave here 2,2′-dinitro-4,4′-bis-(dimethylamino)-diphenylmethane, m.p. 191–193°, as the major product, already described by Ullmann and Maric[15] as melting at 195°.

The nitration was performed by adding 53 g. (0.32 mole) of *m*-nitrodimethylaniline to 660 ml. of 100% nitric acid during a period of one hour, maintaining the stirred solution at 0°. The product was isolated after standing at room temperature for 24 hours by adding water at 10°. The solid which separated was recrystallized from ethylene chloride to give 53 g. (50%) of 2,3,4,6-tetranitrophenylnitramine melting at 145–146° (dec.).

2,3,4,6-Tetranitroaniline was made by the nitration of *m*-nitroaniline using sulfuric and nitric acids essentially in the manner described by Flurscheim[16] who first prepared it.

Picramide was obtained by synthesis from ammonia and picryl chloride, after the manner described for 2,4-dinitroaniline.[17] It was recrystallized from glacial acetic acid for purification.

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(15) F. Ullmann and A. Maric, *Ber.*, **34**, 4315 (1901).

(16) B. Flurscheim, *Z. ges. Schiess, u. Sprengstoffw.*, **8**, 185 (1913); *J. Soc. Chem. Ind.*, **40**, 97 (1921).

(17) F. B. Wells and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 221; see also Beilstein, **12**, 763 (1929).

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[CONTRIBUTION FROM THE UNIVERSITY OF S. CALIFORNIA AND TEMPLE UNIVERSITY]

Determination of the Dipole Moments of Some Derivatives of Hydroxybenzoic Acid[1]

BY CHARLES S. COPELAND AND M. WESLEY RIGG

The dipole moments of several salicylate esters are reported, some of which disagree with previously published values. The dipole moments of a number of additional compounds (recalculated from the original references and compared with the reported values) have been used to calculate a value for the dipole moment of the salicylate esters from group moments. It was found that it is not possible to determine structure in all cases by the use of dipole data. The molecule diethoxymethane was found to exhibit hindered rotation about the O–C–O group. It is shown that small systematic errors in experimental work do not cause a serious error in the calculated value of the dipole moment provided the calculation is made according to the methods discussed.

The effect of hydrogen bonding upon the dipole moment of hydroxy and methoxy benzoic acid esters is of interest since the moment calculated from group values does not agree with the values which have been reported for the salicylate esters.[2] It was also noted[3] that there is generally only a small change in the value of the moments with increase in molecular weight in a homologous series, *i.e.*, the substitution of ethyl or propyl for a methyl group. However, a considerable variation in the reported moments for the salicylate esters was noted. Furthermore, unlike the other phenyl derivatives, the moment of phenyl salicylate is higher than similar derivatives in other compounds. The variation in the values (reported by a number of investigators) for the same compound is also large.

The purpose of this investigation was to verify the reported values of the dipole moments of the salicylate esters, and to determine the dipole moments of a number of additional hydroxy and methoxy benzoates.

Experimental

Dielectric constants were determined by the resonance method, using a frequency of 1200 kilocycles. *Capacitances* were obtained using a General Radio Precision variable condenser (type 772D) in parallel with the experimental condenser consisting of three concentric gold-plated brass cylinders held apart by Pyrex wedges, the inner and outer cylinders being connected by gold-plated brass screws. Its capacitance was found in a series of 28 calibrations over a period of a year to be 50.634 ± 0.77 mmf. *Densities* were obtained by weighing a calibrated glass bob both in air and in the thermostated substance in question with an analytical balance. *Refractive indices* were measured with an Abbe refractometer.

Preparation and Purification of Materials.—*Benzene* was washed with concentrated sulfuric acid, and then with water, dried, and finally fractionally recrystallized three times. It was stored over sodium and distilled off immediately before use. *Methyl, ethyl* and *isopropyl salicylates* and *ethyl benzoate*, *phenyl salicylate* and *methyl p-hydroxybenzoate* were obtained from the Eastman Chemical Co. The first four materials were fractionally distilled under reduced pressure when needed, the middle, constant-boiling fractions being collected and found to contain neither water nor free acid. The last two materials were fractionally crystallized from their melts and then recrystallized from benzene to constant melting points. *Methyl o-methoxybenzoate* and *methyl p-methoxybenzoate* were prepared by treating methyl salicylate or, respectively, methyl *p*-hydroxybenzoate with methyl sulfate in benzene solution and refluxing for several hours. The mixture was washed successively with sodium bicarbonate and dilute sodium hydroxide solutions,

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(1) Presented before the 110th Meeting of the American Chemical Society, September, 1946, in Chicago, Illinois.

(2) C. Hyrnakowski and C. Kalinowski, *Compt. rend.*, **197**, 483 (1933).

(3) Symposium on Dipole Moments, *Trans. Faraday Soc.*, appendix (1934).