stirred for three hours at 25°. The reaction mixture was filtered and the filtrate acidified with *N* hydrochloric acid. The precipitate was collected, washed, dried *in vacuo*, and recrystallized from 30% ethanol to give 1.7 g. (93%) of III, colorless needles, m. p. 186–187°.

Anal. Calcd. for $C_{15}H_{11}O_5NI_2 \cdot H_2O$ (557): C, 32.4; H, 2.4; N, 2.5. Found: C, 32.5; H, 2.7; N, 2.3.

3,5-Diiodo-4-(3′,5′-diiodo-4′-hydroxyphenoxy)-hippuric Acid (IV) —To 0.7 g. of III, dissolved in 10 ml. of 15 *N* ammonium hydroxide, was added, slowly and with stirring, the requisite amount of *N* potassium triiodide. When about half of the iodine had been added, the ammonium salt of IV separated in the form of glistening silvery leaflets. After all of the iodine had been added the solution was stirred for several minutes and allowed to stand at 5° for three to four hours. The suspension was decolorized with sodium metabisulfite and the free acid liberated by the addition of acetic acid. The precipitate was collected, washed with water, and dried *in vacuo* to give 1.0 g. (97%) of IV, colorless crystalline powder, m. p. 248° with decomposition and evolution of iodine. After recrystallization from 70% ethanol IV was obtained as colorless leaflets, m. p. 248° with decomposition.

Anal. Calcd. for $C_{15}H_9O_5NI_4$ (791): C, 22.8; H, 1.1; N, 1.8. Found: C, 22.8; H, 1.5; N, 1.8.

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GATES AND CRELLIN LABORATORIES OF CHEMISTRY
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PASADENA, CALIFORNIA
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The Light Absorption and Fluorescence of Triarylmethyl Free Radicals

BY LINUS PAULING

By working at low temperatures with triarylmethyl free radicals frozen in a rigid glassy solvent, Lewis, Lipkin, and Magel[1] have obtained absorption spectra and fluorescence spectra which show a striking vibrational fine structure, essentially the same for absorption (determined by the vibrational structure of the excited state) and fluorescence (determined by the normal state); the authors report nine vibrational frequencies for the triphenylmethyl radical, and their reproduced microphotometer records indicate one or two more (Table I).

TABLE I

COMPARISON OF VIBRATIONAL FREQUENCIES

Triphenylmethyl Absorption	Triphenylmethyl Fluorescence	Benzaldehyde Raman
190	230	239 cm^{-1}.
(400)[a]		439
600	670	615
820		827
970	970	1001
1090	1080	1164
		1203
1520	1550	1597
	1850	
	2210	
	2510	
		3063

[a] Estimated from the published microphotometer record.

It may be noted that an interesting correlation exists between these absorption and fluorescence spectra of triphenylmethyl and the Raman spectra of substituted benzenes. The principal Raman frequencies of substituted benzenes are 200, 400, 615, 1000, 1165, 1595, and 3060 cm.$^{-1}$; all but the last (the carbon–hydrogen stretching frequency) are represented in the absorption and fluorescence spectra. The correlation is closest with monosubstituted benzenes containing a group conjugated with the benzene ring, such as methyl benzoate and benzaldehyde; Raman frequencies for benzaldehyde (other than the carbonyl frequency 1700 cm.$^{-1}$) are given for comparison in Table I. There is a rough correlation in intensity as well as in frequency.

The bands at 1850, 2210, and 2510 may be combinations or overtones; they may well be combinations of the important frequency 1550 cm.$^{-1}$ with lower frequencies. The failure of the band with shift 3063 cm.$^{-1}$ to appear in the fluorescence spectrum may indicate that the coupling of this C–H vibration with the electronic transition is very weak.

An interesting detail is the gradual change in shape of the absorption spectrum in the 1000–1200 cm.$^{-1}$ region as the phenyl groups in the triphenylmethyl radical are successively replaced by *p*-*t*-butylphenyl groups. The band at 1000 cm.$^{-1}$ gradually diminishes in intensity, and finally disappears; the spectrum of tri-(*p*-*t*-butylphenyl) methyl, which otherwise closely resembles that of triphenylmethyl, shows a single peak at 1120 cm.$^{-1}$ in place of the 970–1080 doublet. This fact is without doubt related to the observed characteristic absence of the lines near 1000 cm.$^{-1}$ in the Raman spectra of the para-disubstituted benzenes.

I believe that measurements of well-resolved absorption spectra, fluorescence spectra, and phosphorescence spectra of rigid solutions at low temperatures may provide much useful information about the vibrational frequencies of molecules of dyes and other substances which could not be readily obtained by the techniques of Raman and infrared spectroscopy.

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The System Sodium Molybdate–Sodium Nitrate–Water and Part of the System Sodium Molybdate–Molybdic Oxide–Water, at 25°

BY J. E. RICCI AND L. DOPPELT[1]

The experimental procedure for these measurements was that described for similar investigations of ternary systems of salts and water. The materials used were C. P. products throughout, the molybdic oxide being a very pure sample,[2] found

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[1] G. N. Lewis, D. Lipkin, and T. T. Magel, THIS JOURNAL, **66**, 1579 (1944).

[1] Present address: U. S. Army.

[2] This material, resublimed and of stated purity 99.97%, was the gift of the Climax Molybdenum Company.