510. *Micro-determination of the Molecular Weights of Picrates by a Spectrophotometric Method.*

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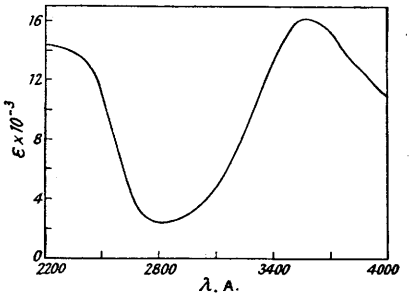
A method is described for the determination of the molecular weight of a picrate by an examination of its light absorption in the ultra-violet region of the spectrum. The determination is carried out with approximately 2 mg. of the picrate, the accuracy being of the order of ±2%.

ETHANOLIC solutions of picric acid exhibit high-intensity absorption between 2000 and 2500 A., and between 3500 and 4000 A. (figure). Few colourless organic compounds show absorption of appreciable intensity between 3500 and 4000 A. These two facts led us to investigate the possibility of determining molecular weights of bases and hydrocarbons by the measurement of the intensity of light absorption of their picrates within the region 3500—4000 A. By using a Unicam photoelectric spectrophotometer of the compensating-cell type, the light absorption characteristics of a number of picrates were examined. Table I lists the observed intensity of absorption of these picrates at 3800 A., a wave-length chosen from the high-intensity band of



picric acid (3400—4000 A.), at a point remote from the region 2000—3500 A., in which high-intensity absorption is frequently observed in colourless compounds. This choice is to a certain extent arbitrary, similar results to those described being obtained by measurement of the intensity of absorption at other wave-lengths within the high-intensity band of picric acid.

TABLE I.

Picrate.	c (mg./100 ml.).	$\log (I_0/I)_{3800}$.	ε_{3800}.
Ethanolamine	1·109	0·512	13,390
Piperidine	1·090	0·469	13,510
Morpholine	1·462	0·620	13,400
2-Aminopyrazine	1·137	0·472	13,450
N-Ethylaniline	1·196	0·459	13,430
Picric Acid	1·107	0·650	13,450

Apart from the weighing operation, the accuracy of the determination depends upon the high sensitivity of the photoelectric spectrophotometer, the value of log (I_0/I) being repeatedly reproducible with an accuracy of $\pm 1{\cdot}0\%$. The average value of ε_{3800} for the five picrates listed in Table I is 13,440, in excellent agreement with the observed value for picric acid. As required by the constant value observed for ε_{3800}, it was found that the bases corresponding to the picrates listed in Table I show no appreciable absorption at 3800 A.

By assuming the average value 13,440 for ε_{3800}, the molecular weights of a number of picrates were determined by the spectrophotometric method, the relationship $M = 13{,}440Cn/\log(I_0/I)$ being used where n is the molar ratio of picric acid : base or picric acid : hydrocarbon in the picrate, and C is measured in g./l. The values obtained for a number of monopicrates, matched quartz cells of 1 cm. thickness being used, are shown in Table II; whole-number atomic weights were employed.

TABLE II.

Picrate.	c (mg./100 ml.).	log $(I_0/I)_{3800}$.	M, found.	M, calc.	Error, %.
Acenaphthene	2·801	0·990	380	383	−0·8
1-Bromonaphthalene	1·353	0·420	433	436	−0·7
2-Methoxynaphthalene	1·161	0·401	389	387	+0·5
2 : 5-Dichloroaniline *	1·421	0·485	394	391	+0·8
Quinoline	1·319	0·491	361	358	+0·8
8-Hydroxyquinoline	1·388	0·498	375	374	+0·3
Adenine	1·361	0·500	366	364	+0·5
2-Methylpyridine	1·165	0·490	320	322	−0·6
1-Methylmorpholine	1·300	0·525	333	330	+0·9
4-Methylglyoxaline	1·959	0·850	310	311	−0·3
Carbazole	1·327	0·443	403	396	+1·8
Cocaine	2·159	0·550	528	532	−0·8
Narcotine	2·938	0·615	642	642	0·0
Strychnine	2·481	0·598	558	563	−0·9
Vomicine	2·530	0·558	609	609	0·0

* 2 : 5-*Dichloroaniline picrate* separates from water as needles, m. p. 86° (Found : C, 37·0; H, 2·3; N, 13·9. $C_6H_5NCl_2,C_6H_3O_7N_3$ requires C, 36·8; H, 2·1; N, 14·3%).

A determination of the molecular weight of cordycepin, a metabolic product isolated from cultures of the mould *Cordyceps militaris* (Linn.) Link, was carried out by using its monopicrate, with the following result :

	c (mg./100 ml.)	log $(I_0/I)_{3800}$	M
Cordycepin picrate	1·036	0·288	483

This value corresponds to a molecular weight of 254 for cordycepin, which is in close agreement both with that of 247 ± 10 obtained by the X-ray crystallographic method by Mrs. Dorothy Hodgkin and Dr. G. J. Pitt, and with that of 251 required by $C_{10}H_{13}O_3N_5$ subsequently shown by analytical and degradative examination to be the molecular formula of cordycepin (Cunningham, Hutchinson, Manson, and Spring, *J.*, 1951, 2299; Bentley, Cunningham, and Spring, *J.*, 1951, 2301).

The accuracy of this method of molecular-weight determination is dependent upon the exact determination of the molecular extinction coefficient at the chosen wave-length. A small error in the wave-length determination mechanism of the instrument employed may lead to an appreciable error in the value of ε. It has been our experience that such variations can occur (the value $\varepsilon_{3800} = 13{,}200$ was obtained as the average for 12 picrates examined in a second spectrophotometer similar to the one described above). For this reason it is desirable that the spectrophotometer employed for molecular-weight determination should be standardised against a number of picrates of known molecular weight, matched quartz cells being used in the same aspect.

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