The ratio of the atomic weight of each element to that of the next preceding (also succeeding) zero-group element is computed. The ratio of the corresponding atomic numbers is also obtained and the difference between these two ratios is plotted against the atomic numbers of the elements. These graphs for Rows 1, 2, 3, 4 and 6 of the periodic chart are rather irregular and could not be used with much confidence for the prediction of atomic weights. Fortunately, there are no unknown atomic weights for the elements in these rows of the chart. For the remaining rows of the chart the graphs exhibit a considerable degree of regularity and the differences between the two ratios A_x/A_0 and N_x/N_0 become smaller as the atomic numbers increase. Indeed, for the last row in the chart this difference is close to zero. These graphs are shown in the accompanying figure. The estimated loci of the points for the elements whose atomic weights have not been experimentally determined are shown on the dotted portions of the graphs. From these estimated points it is obvious that the missing atomic weights can be computed by reversing the calculation. The "best" values thus estimated are given in Table I.

TABLE I

ESTIMATED ATOMIC WEIGHTS

Symbol	Name	At. no.	At. wt., estimated
Ma	Masurium	43	97.5? (or 98.8)
Il	Illinium	61	146.0
Re	Rhenium	75	187.4
	Eka-iodine	85	212
	Eka-cesium	87	223
Ac	Actinium	89	229
Pa	Proto-actinium	91	234

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 9]

ABSORPTION COLORS OF THE SECOND ORDER

BY JEAN PICCARD

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Some years ago Piccard and Kharasch isolated *p*-nitrosotriphenylamine and explained its orange color as a color of the second order. We may here briefly review the theory of absorption colors of the second order. As a rule, any increase of the molecular weight of a colored organic compound shifts its color in a definite direction, that is, from yellow to orange to red to violet to blue, and finally to green. If we increase the molecular weight still more, this green color turns to yellowish-green and then to yellow. As this phenomenon reminds us of the interference colors of the

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[1] Piccard and Kharasch, THIS JOURNAL, 40, 1074 (1918).

second order we gave these new colors the name of absorption colors of the second order.[2] This regular development of colors does not stop at the yellow, but we were able to proceed until an orange of the second order had been obtained and we have now reached a red, which is even tinged with violet. During these investigations my collaborators and I were obliged to prepare many new organic bases of very high molecular weight, the last one being tetrabiphenylbenzidine, $C_{60}H_{44}N_2$. These compounds will be described in a following paper.

It was, of course, desirable to find a theory for the formation of the colors of the second order. The following explanation is obvious: the color of ordinary yellow dyes is produced by an absorption band or a group of bands, entering the spectrum from the violet end. When the violet light is absorbed we observe its complementary color, yellow; when the absorption band goes into the blue, we see orange and so on until the band has reached the red end of the spectrum and the dye becomes green. If by further increase of the weight we produce a further shifting of the band, it will leave the visible part of the spectrum. Experience shows that in this case we do not obtain a colorless compound, but that a new band, which is the "octave" of the first one, always enters the visible part of the spectrum at its violet end and we then get the yellow of the second order.

To prove the correctness of this theory we had to show first that the described phenomenon is not merely accidental. For this purpose we prepared numerous dyes showing colors of the second order and there is now no doubt that from an empirical point of view our theory has been successful. From a theoretical point of view, however, it was very desirable to prove that the absorption band which we had seen disappearing at the red end of the spectrum has really entered the infra-red.

The observation of the infra-red spectrum is a rather difficult task and I am grateful to Professor Victor Henri at the University of Zürich for helping me with much advice, as well as for allowing me to work as a guest in his Laboratory and to use his apparatus for this investigation. The result of this work was a very striking one: all of our dyes showing colors of the second order have an exceedingly strong absorption band in the infra-red at a place in the spectrum where other organic and inorganic compounds, even those that are known for their strong absorption of infra-red light, have no absorption at all or only a very slight one. This place is the part of the spectrum which is the nearest to the visible red light about $\lambda = 0.8$ to 1.0μ.

These investigations are far from being concluded, but they have shown clearly the importance of the examination of this part of the spectrum. One special case should be reported here, a case in which the examination of the infra-red spectrum of a dye allows us to draw conclusions as to its constitution.

[2] Piccard, *Ber.*, **46**, 1843 (1913).

Auramine.—The constitution of auramine has often been discussed and quite a number of investigators have been inclined to give to this yellow dye a quinonic formula. If this compound really has a quinonic constitution, it should have a relatively deep color.[3] There has, however, been only one explanation offered as to why auramine, although being quinonic, should be only yellow,—its classification among the colors of the second order. In this case, as can easily be seen, the examination of the infra-red spectrum is the means of deciding the controversy. Our observations show that auramine does not absorb in the infra-red at $\lambda = 0.8$ to 1.0μ, hence it is not a dye of the second order. Therefore, it cannot be quinonic and its constitutional formula[4] is $[(CH_3)_2N—C_6H_4—C(=NH_2)—C_6H_4—N(CH_3)_2]Cl$.

I wish to thank my collaborator, Dr. L. Marton of Zurich, for his valuable help.

Summary

Our first definition[2] of absorption colors of the second order was as follows: if a compound belongs to a family of colored compounds, the color of which has (as a result of progressive changes) already gone through the ordinary succession from yellow through red and blue to green, and if by further alteration of the molecule in the same sense as the one which had produced this shift of colors we obtain again the same succession of colors beginning with yellow, we call these colors "absorption colors of the second order."

Now, after having studied the infra-red spectrum of numerous dyes of the second order, we can give another and simpler definition: any colored compound has a color of the second order if it has a strong absorption in the infra-red next to the visible part of the spectrum.

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[3] Semper, *Ann.*, **381**, 234 (1911).

[4] We have given up entirely the old-fashioned formulas with quinquivalent nitrogen, chiefly because they are based on an hypothesis without the slightest proof, whereas Werner's coördination formula of ammonium chloride and substituted ammonium chlorides does not pretend anything more than the well-warranted fact that there are in solution two ions, one $[NR_4]$ and one Cl ion. In order to make the formula more lucid we use N to indicate the nitrogen atom which has saturated its fourth coördination place by addition of the hydrogen ion of the acid (or an alkyl which takes its place). See also Piccard and Dardel, *Helvetica Chim. Acta*, **4**, 414 (1921).