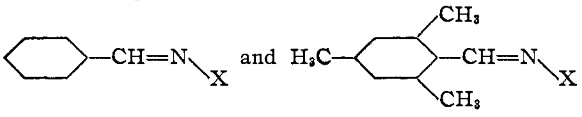
Absorption Spectra of Some Benzal and Mesitylal Schiff Bases

BY LLOYD N. FERGUSON AND JOHN K. ROBINSON

When considering the relative light absorptions of two compounds such as



where X is any simple group, it is difficult to predict whether the steric effect of the *ortho* methyl groups in the mesityl compound will decrease absorption from that of the simple phenyl compound or whether there will be an increase in absorption due to hyperconjugation of the methyl groups. For this reason, the spectra of several Schiff bases of benzaldehyde and mesitylaldehyde were measured. The spectral characteristics are listed in Table I.

TABLE I

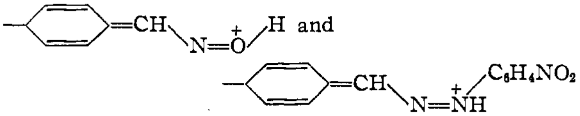
SPECTRAL CHARACTERISTICS OF SOME BENZAL AND MESITYLAL SCHIFF BASES

	Oxime		*p*-Nitrophenylhydrazone		Ethylenediamine	
Compound	λ_m (mμ)	ϵ_m	λ_m (mμ)	ϵ_m	λ_m (mμ)	ϵ_m
Benzal	252	14,300	407	34,200	247[1]	29,000[1]
Mesitylal	252	9,400	411	31,700	264	8,100
Difference	0	4,900	4	2,500	17	20,900

From these results, it is observed that there are no significant differences between the wave lengths of maximum absorption of the two oximes or of the two *p*-nitrophenylhydrazones. In going from dibenzalethylenediamine to dimesitylalethylenediamine there is a bathochromic effect. This, perhaps, is due to the hyperconjugation of the methyl groups becoming more prominent since the chromophoric system is double. Actually upon constructing the Fisher–Hirschfelder models of these three classes of compounds there appears to be only a small steric hindrance between the mesityl methyl groups and the group X.[2]

It has been observed before[3] that small steric hindrances have little effect upon $\lambda_{\max.}$ but do decrease $e_{\max.}$. This is illustrated in the present case by the oximes and the ethylenediamines. It is noted that this effect is very small in the case of the nitrophenylhydrazones; however, this is understandable. The nitrophenylhydrazones have absorption bands near 400 mu[4] without the aid of the phenyl or mesityl groups at the other end of the molecule, and consequently steric hindrance does not affect appreciably the molecular extinction.

The only explanation offered at this time for the trend in the differences of $\lambda_{\max.}$ is to say that forms such as



contribute to the resonances of benzaldoxime and benzal-*p*-nitrophenylhydrazone. Such forms would be opposed by the hyperconjugation of the methyl groups in the mesityl nucleus. It may be that the two effects just cancel one another in the mesitylaldoxime, that the hyperconjugation is slightly more effective than the opposing resonance in the mesitylal-*p*-nitrophenylhydrazone and that in the ethylenediamine compounds, where the corresponding resonant forms cannot exist and the chromophoric system is double, the hyperconjugation causes a much larger bathochromic effect.

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[1] Taken from Ferguson and Branch, THIS JOURNAL, **66**, 1467 (1944).

[2] O'Shaughnessy and Rodebush found the steric interference between the *ortho* methyl groups and the carbonyl oxygen of 2,4,6-trimethylacetophenone to be hardly strong enough to prevent a coplanar configuration, *ibid.*, **62**, 2910 (1940).

[3] O'Shaughnessy and Rodebush, *ibid.*, **62**, 2910 (1940).

[4] Ferguson and Battle, Report presented before the Organic Division of the Washington Chemical Society, Oct., 1948, at Washington, D. C.

Comparison of Age with the Relative Abundance of Argon and Potassium in Rocks

BY R. L. FARRAR, JR., AND GEORGE H. CADY

The study reported in this communication was done as a test of the proposal of Thompson and Rowlands[1] that the accumulation of argon resulting from decay by K electron capture of K^{40} should serve as a measure of the age of rocks containing potassium. For this study solid rocks of known geologic age were kindly furnished by G. E. Goodspeed of our Department of Geology.

The analytical procedure involved the following steps: (1) A 60-g. sample of sodium carbonate was freed of argon by pumping away gas for three hours from the molten salt held in a stainless steel vessel at about 950°. (2) Argon and other gases were removed from the surface of a 10-g. sample of rock composed of pea-sized pieces by allowing the material to stand for about an hour at room temperature in a vacuum. (3) The rock was then dissolved in the sodium carbonate at 950 to 1000°. This process was allowed to continue for a twenty-four-hour period to secure complete liberation of rare gases. (4) He + Ne and A + Kr + Xe were determined in the gas, using methods previously described by Cady and Cady.[2] Since spectroscopic tests showed that not more than traces of Ne, Kr or Xe could have been present in each case, the results of the analyses are reported in the table as helium and argon, respectively. (5) Potassium was determined in the mass resulting from the sodium carbonate fusion.

Conclusions: (1) These analyses indicate no regular increase of the A/K ratio with age. (2) The range in argon content is much less than that of helium. (3) Most of the argon in at least the first two samples probably originated from a source, perhaps the atmosphere, other than the

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[1] F. C. Thompson and S. Rowlands, *Nature*, **152**, 103 (1943).

[2] G. H. Cady and H. P. Cady, *Ind. Eng. Chem., Anal. Ed.*, **17**, 760 (1945).