

Medium	Refractive index	θ (liquid)/ θ (air)
Water	1.33	1.36 (1.31)
Ethyl ether	1.35	1.44 (1.39)
Ethyl alcohol	1.36	1.42 (1.37)
Xylene	1.50	1.50 (1.44)
Benzene	1.50	1.53 (1.47)
Nitrobenzene	1.55	1.50 (1.44)
Carbon disulphide	1.63	1.65 (1.59)

A high accuracy should not be expected from these preliminary observations, since the angles of deflexion of the suspension under radiation pressure are only of the order of 10^{-5} radian; errors up to 10 per cent are to be expected from Brownian and other disturbances. The deflexion ratios should be corrected for the reflexion loss between the glass window of the suspension tube and the liquid inside, this loss being less than when air is inside, by 3-4 per cent; the corrected figures are given in brackets. No allowance has been made for a possible change in the reflectivity of the vane when in a refracting liquid.

Within the limits of its present accuracy, the experiment appears to confirm the theoretical expectation that the radiation pressure increases in a refracting medium in proportion to the refractive index.

R. V. JONES

Department of Natural Philosophy,
University of Aberdeen.

Dec. 16.

¹ Lebedew, P., *Ann. der Phys.*, **6**, 433 (1901).

² Nichols, E. F., and Hull, G. F., *Phys. Rev.*, **2**, 26 (1903).

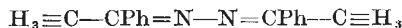
³ Barlow, G., *Proc. Roy. Soc., A*, **87**, 1 (1912).

⁴ Tear, J. D., *J. Opt. Soc. Amer.*, **11**, 135 (1925).

Hyperconjugation and Light Absorption

THE replacement of the hydrogen of a methine group in a number of conjugated organic compounds by an alkyl radical causes a batho- or hypsochromic shift in the principal absorption maxima. This effect is particularly noticeable in methyl substitution, and could be explained by the hyperconjugation introduced by the methyl group.

There is a hypsochromic shift of 300 Å. in the absorption maximum of phenyl methyl ketazine on that of benzylideneazine¹, due to the contribution of a shorter conjugated form:

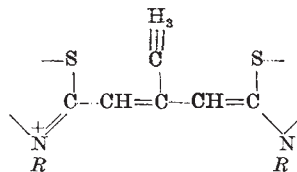


to the total resonance system.

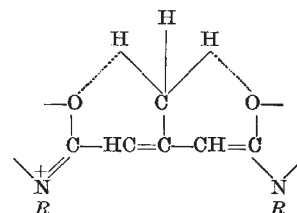
The absorption maximum of the 2:4 dinitrophenylhydrazone of acetaldehyde in ethanol shows a bathochromic shift of 120 Å. on that of its formaldehyde homologue. The three consecutive higher homologues show, however, a bathochromic shift of only 90 Å., which is 30 Å. less². The large bathochromic shift given by the acetaldehyde derivative could be explained on the basis of an extension of the conjugated chain through the hyperconjugation of the methyl group, which effect is felt to a less degree in the homologues.

The absorption maxima of thia- and selenocarbocyanines with an alkyl group substituted in the central position of their three-carbon methine chain show a hypsochromic shift on those of the unsubstituted compounds. This shift is, again, most pronounced with the methyl substituent³. In a system of

this type, a possible contribution to resonance would be that of the shorter and less-charged conjugated chains extending from the nitrogen of the heterocycle to the methyl group:



This hypsochromic shift does not appear in the oxacarbocyanines³, in which there is the possibility of an annullment of the hyperconjugative effect of the alkyl group because of hydrogen bonding between the alkyl group and the oxygen of the heterocycle, leading to the formation of a six-membered ring:



The effect of alkyl substitution in oxacarbocyanines on light absorption is that of weighting the molecule, and therefore only a small bathochromic shift of the absorption maxima is observed.

The hypsochromic effect cannot be ascribed to steric hindrance. Neither in the azines nor in the cyanines is the methyl substitution in the methine chain likely to force the systems out of their coplanar configuration^{1,4}. Also, in the cyanines the introduction of substituents on the central atom of the three-carbon methine chain does not depress the sensitizing action³.

It is significant that with the 2:4-dinitrophenylhydrazones² and with the simple thia- and selenocarbocyanines³, the shift of the maxima brought about when an ethyl or higher alkyl group is introduced is approximately three-quarters of the shift caused by replacing the hydrogen atom by a methyl group. A similar ratio applies to the hyperconjugative effect of *p*-methyl and *p*-ethyl substitution on the hydrolysis of benzhydryl chloride^{4,5}.

A detailed investigation is now in progress on the influence of substitution of this nature on the light absorption of conjugated compounds.

M. PIANKA
H. C. BARANY
C. G. SMITH

Northern Polytechnic,
London, N.7.
Nov. 10.

¹ Barany, H. C., Braude, E. A., and Pianka, M., *J. Chem. Soc.*, 1898 (1949).

² Braude, E. A., and Jones, E. R. H., *J. Chem. Soc.*, 499 (1945).

³ Brooker, L. G. S., and White, F. L., *J. Amer. Chem. Soc.*, **57**, 2480 (1935).

⁴ Hughes, E. D., Ingold, C. K., and Taher, N. A., *J. Chem. Soc.*, 955 (1940).

⁵ Arnold, R. T., Murai, K., and Dodson, R. M., *J. Amer. Chem. Soc.*, **72**, 4193 (1950).

⁶ Blout, E. R., Eager, V. W., and Gofstein, R. M., *J. Amer. Chem. Soc.*, **68**, 1983 (1946).