

The Nature of the Long-wavelength Absorption Bands of Simple Unsaturated Chromophores

By S. F. MASON and G. W. VANE

(School of Chemical Sciences, University of East Anglia, Norwich)

It has been shown¹ that the $n \rightarrow \pi^*$ transition responsible for the 3000Å absorption of the carbonyl group has a magnetic moment of one Bohr magneton (β_M) and that the transition in formaldehyde involves the displacement of charge to the π^* -orbital of the carbonyl group from the C-H σ -bonds as well as the lone-pair of the oxygen atom. Recently Berry suggested,² by analogy, that the long-wavelength shoulder in the spectrum of the isoelectronic molecule, ethylene, is due to a similar transition in which charge is displaced to the antibonding π_y^* -orbital from the highest occupied σ -molecular orbital, which has π_x symmetry. Such a transition, and its analogues in other simple unsaturated chromophores, should have a magnetic moment and, in a dissymmetric

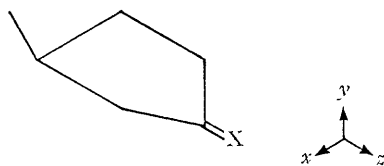
molecular environment, a non-zero rotational strength.

The present work reports the absorption and circular dichroism spectra (Figure) of the olefin (I) ($[\alpha]_D^{22} = +15.6^\circ$), the imine (II) ($[\alpha]_D^{19} = +41^\circ$), and the phosphorane (III) ($[\alpha]_D^{21} = +42^\circ$). These isomers were prepared by standard methods from the ketone (IV) which has an $n \rightarrow \pi^*$ transition with a relatively large rotational strength, so that an analogous transition in (I), (II), or (III) should give a readily detectable circular dichroism. The results show (Figure) that the low-energy band of the olefin (I) at 46,000 cm^{-1} is devoid of measurable optical activity although the $\pi_y \rightarrow \pi_y^*$ transition gives a circular dichroism absorption with an onset at 45,000 cm^{-1} . Similarly, the low-energy

¹ S. F. Mason, *Mol. Phys.*, 1962, 5, 343.

² R. S. Berry, *J. Chem. Phys.*, 1963, 38, 1934.

transition of the phosphorane (III) (absorption λ_{\max} 4165 Å, ϵ_{\max} 2200, in iso-octane) gives no measurable circular dichroism. A low-energy rotational strength one and two orders of magnitude smaller than that of (IV) would have been detectable experimentally for (III) and (I), respectively.



- (I) X = Me₂C
 (II) X = BuⁿN
 (III) X = Ph₃P
 (IV) X = O

The low-energy transition of the imine (II), on the other hand, has a rotational strength with the same sign and one-half as large as that of the ketone (IV). As in the case of the thiocarbonyl chromophore,³ the comparison indicates that the long-wavelength band of the imine chromophore is due to an $n \rightarrow \pi^*$ transition with a magnetic moment of $\sim 0.5 \beta_M$. It is concluded that, of the several chromophores studied, only those with classical non-bonding electrons, the thiocarbonyl³ and the imine group, give a low-energy $n \rightarrow \pi^*$ transition analogous to that of the carbonyl group

although the highest-occupied molecular orbital, like that of formaldehyde,⁴ probably embodies a significant contribution from the σ -bonding orbitals. The low-energy transitions of (I) and (III) have a different origin, and that of the olefin (I) is probably polarized perpendicular to the C=C bond, for if the transition were z -polarized it would mix with the adjacent $\pi_y \rightarrow \pi_y^*$ transition and acquire part of the finite rotational strength of the latter.

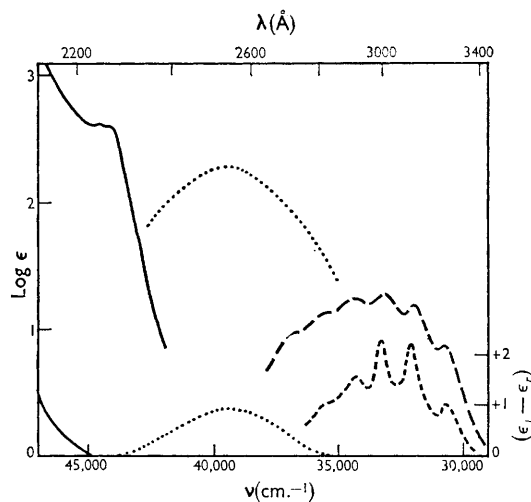


FIGURE. The circular dichroism (lower curves) and absorption spectrum (upper curves) of — the olefin (I), the imine (II), and - - - the ketone (IV).

(Received, September 13th, 1965; Com. 580.)

³ R. E. Ballard and S. F. Mason, *J. Chem. Soc.*, 1963, 1624.

⁴ J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, 1960, **32**, 303; P. L. Goodfriend, F. W. Birss, and A. F. Duncan, *Rev. Mod. Phys.*, 1960, **32**, 307.