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COUPLED CHROMOPHORES - PART I
INTERACTION IN SOME STEROIDAL γ- NITROKETONES

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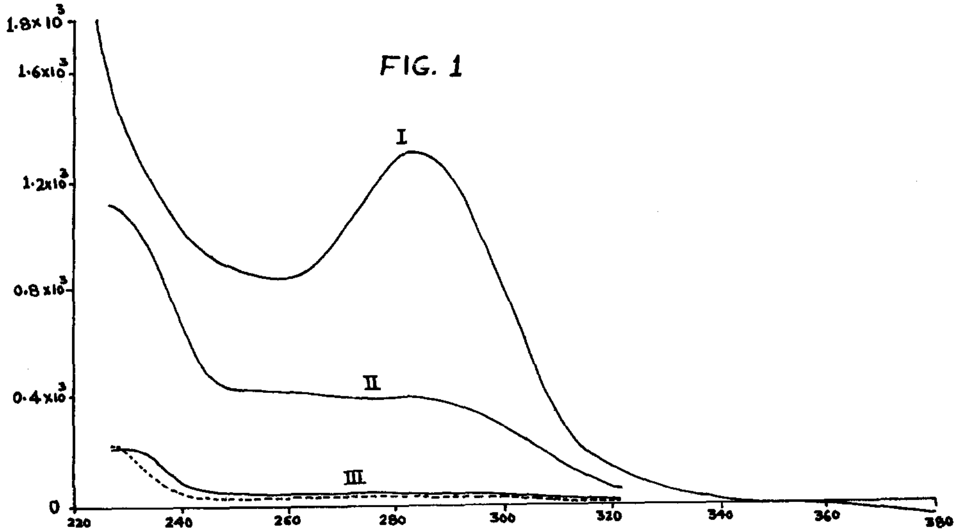
Intensification of certain bands and other deviations from additivity have often been observed in absorption spectra of molecules having non-conjugated chromophores suitably placed for coupling (1-6). In the U.V. spectrum of the nitroketone I(7) we have found more than a twenty-fold increase in the extinction coefficient of the band in 283 nm region. In the isomeric ketone II this effect is less marked. Here a steric interaction between C-18 and C-21 methyl groups opposes that orientation of the side chain which places the nitro group nearest to the carbonyl function. The stereochemistry of these compounds seems specially conducive to interaction as the spectrum of the open chain model III is not anomalous (Fig.1). In the shorter wave length region also the same order of absorption (I > II > III) is observed (8).

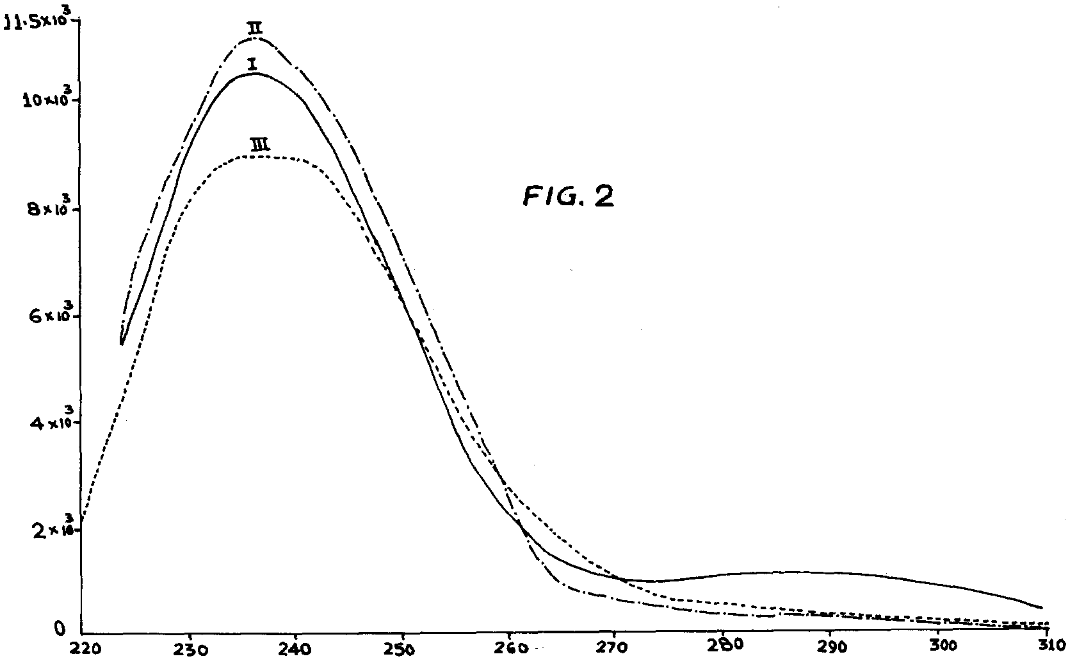
In going from ethanol to chloroform the 283 nm band in I shows no appreciable solvent shift expected for a $n \longrightarrow \pi^*$ transition (nitro or carbonyl). Either the ground and excited states are raised the same amount by change of solvent or neither state is effected at all. Perhaps the lone-pair electrons are less accessible to solvent due to proximate interacting group (2). Ultraviolet spectra of I, II, and III taken in alkaline medium, are shown in Fig. 2. In the long wave length region a maximum (ε >1000) is seen only in I, although a moderate intensity increase is evident in II also (9). Since simple nitro alkane anions do not show any peaks in this region (10),

FIG. 1

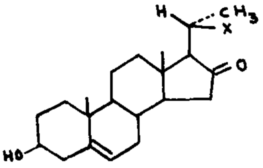


U.V. SPECTRA TAKEN IN ETHANOL; --- COMPUTED FOR EQUIMOLAR MIXTURE OF NITROMETHANE AND ACETONE FROM INDIVIDUAL SPECTRA

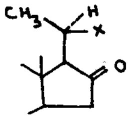
FIG. 2



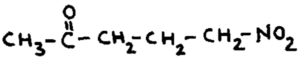
U.V. SPECTRA TAKEN IN 1:1 MIXTURE OF ETHANOL AND 0.1N SODIUM HYDROXIDE SOLN.



I, X = CH_2NO_2
IV, X = CN



II, X = CH_2NO_2
V, X = CN



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-NO_2$

III

the enhancement observed here may be attributed to a carbonyl transition.

Many aspects of theory of coupled chromophores, like the role of charge transfer states in intensification of n $\rightarrow\pi$ transition, are not fully settled and examples with new features can be useful. In the nitroketone I the chromophores are separated by more than three sigma bonds and, therefore, should be coupled directly (11). For such a system this seems to be the first example with dramatic intensity enhancement.

Unusually strong $\Delta\varepsilon$ values may be observed in CD when interaction between functions results in an inherently dissymmetric chromophore (1, 2,12). The dichrograms of I and II, however, are quite similar to those of simple C-16 oxosteroids (13). This situation can obtain if the involved orbitals are perturbed in such a way as not to produce a sufficient component (4) of electric dipole transition moment ($\overrightarrow{\mu_e}$) along the direction of magnetic dipole transition moment ($\overrightarrow{\mu_m}$). Alternatively, an opposite contribution from the nitro function can cause levelling of the carbonyl cotton effect (13).

Moderate enhancement of intensity in the $n \rightarrow \pi^*$ transition region was also observed in the UV spectrum of cyano ketone IV ($\varepsilon_{283} \sim 175$) but not in that of V ($\varepsilon_{283} \sim 64$). The unique stereochemistry (14) of this steroidal system seems to afford opportunity for study of coupling between different functionalities and more compounds of this type are currently being synthesised.

REFERENCES

1. R.C. Cookson, Proc. Roy. Soc. (London), A297, 27 (1967); A Moscowitz, Proc. Roy. Soc. (London), A297, 40 (1967).
2. H.H. Jaffe and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, p. 437. John Wiley and Sons, Inc. New York, N.Y. (1962).
3. G.P. Kugatova- Shemyakina and G.M. Nikolaev, Tetrahedron, 23,2987 (1967).
4. A. Moscowitz, K. Mislow, M.A.W. Glass and C. Djerassi, J. Am. Chem. Soc., 84, 1945 (1962).
5. H. Labhart and G. Wagniere, Helv. Chim. Acta, 42, 2219 (1959).
6. R.C. Cookson and J. Hudec, J. Chem. Soc., 429 (1962).
7. S.V. Kessar, Y.P. Gupta, R.K. Mahajan and A.L. Rampal, Tetrahedron, 24, 893 (1968).
8. Bathochromic shift or increased absorption for short wavelength carbonyl and/or nitro bands is indicated, although the maximalie below our instrument range. A red shift of $\pi \rightarrow \pi^*$ band is not conclusive evidence for a' charge transfer ' transition (1).
9. From t.l.c. examination, in a number of solvent systems, it was concluded that nitro ketone I can be recovered essentially unchanged by careful acidification of its alkaline solution.
10. F.T. Williams, Jr., P.W.K. Flanagan, W.J. Taylor and H. Schechter, J.Org. Chem., 30, 2674 (1965).
11. Interaction involving central sigma orbitals (1) is difficult to visualise.
12. G. Snatzke, J. Chem. Soc., 5002 (1965).
13. We are thankful to Dr. Snatzke for CD determinations. A detailed discussion of this and CD of some related compounds is deffered.
14. Y. Mazur and F. Sondheimer, Experientia, 16, 181 (1960).