Monatshefte für Chemie 131, 309–311 (2000)

**Monatshefte für Chemie**
**Chemical Monthly**

Printed in Austria

*Short Communication*

# Induction of Wavelength Dependent Photochemistry in Bilirubins by Serum Albumin [1]: A Comment

**Gordon J. Troup**[1,*] and **Riccardo Pratesi**[2]

[1] Physics Department, Monash University, Clayton, Victoria 3168, Australia
[2] Dipartimento di Fisica, Università di Firenze, I-50100 Firenze, Italy

**Summary.** The article cited in the title [1] did not take into account the probability of occupation of the exciton (*Davidoff*) states by the different chromophores of the bilirubins, as is determined by the necessary quantum mechanics. Since this probability is intrinsically wavelength dependent, the discussion in the mentioned paper should be extended with respect to this effect.

**Keywords.** Bile pigments; Exciton coupling.

## Introduction

We wish to point out that the lack of detailed exciton photophysics in Ref. [1] militates against a possible quantification and renders some of the explanations rather incomplete. To justify this, a brief account of exciton (*Davidoff*) coupling as introduced in Ref. [2] and further developed in Ref. [3] should be given.

Consider a molecule with two dissimilar chromophores $i$ and $j$; the dissimilarity may originate either from intrinsic chromophore structure (*e.g.* asymmetric bilirubin (*BR*) in methanol/ammonia solution), or from an originally identical chromophore interacting with another molecule (symmetric *BR*s in serum albumin). Let their excited states before applying the exciton coupling (parameter $V(ij)$) be $|i\rangle$ and $|j\rangle$ where $|j\rangle$ has the higher energy $E(j)$ and $|i\rangle$ the lower energy $E(i)$. Then the exciton states $|\alpha\rangle$ and $|\beta\rangle$ with $E(\beta) > E(\alpha)$ will be given by $|\beta\rangle = c|i\rangle + s|j\rangle$ and $|\alpha\rangle = s|i\rangle - c|j\rangle$ where $c = \cos$, $s = \sin$, and $s > c$. Thus, the higher energy exciton state is always preferentially occupied by the higher chromophore energy state as predicted by perturbation theory. Variation of $c$ (and therefore of $s$ because of $s^2 + c^2 = 1$) has been expressed as a function of $((E(j) - E(i))/2V(ij))$ [3].

---

[*] Corresponding author

The probability of absorption of radiation of wavelength $\lambda$ by the exciton state $|\beta\rangle$ is proportional to its lineshape $I(\beta, \lambda)$. $I(\beta, \lambda)$ must be multiplied by $s^2$ to obtain the probability of the radiation ending up in chromophore $j$ *via* absorption by $|\beta\rangle$. The total probability of the energy ending up in chromophore $j$ is therefore proportional to $s^2 I(\beta, \lambda) + c^2 I(\alpha, \lambda)$, which is clearly dependent on the wavelength. It is precisely this important piece of photophysics which has been omitted in Ref. [1].

## Results and Discussion

To obtain the final probability of the photoproduct quantum yield, $s^2 I(\beta, \lambda)+ c^2 I(\alpha, \lambda)$ must be multiplied by the probability $p(\lambda)$ of the photoproduct formation once the energy has been taken up by the chromophore. However, only $p(\lambda)$ has been discussed in Ref. [1], with an unquantified reason being given for its wavelength dependence. If this dependence is small or nonexistent, it is obvious that the asymptotic quantum yields will be determined by $s^2$ and $c^2$.

The asymptotic ratios of photoproduct quantum yields for chromophores $i$ and $j$ are $(s^2/c^2)$ for $j$ and $(c^2/s^2)$ for $i$ as the wavelength changes under the above conditions. Hence it is possible to calculate $s^2$ and $c^2$. For example, if $(s^2/c^2)$ equals 2:1, $s^2 = 0.66$ and $c^2 = 0.33$. All cases discussed in Ref. [1] have the photoproduct quantum yield changed by a factor less than 2, so the discussion and the diagram identifying exactly one chromophore state with an exciton state are poor approximations in this regime.

Further, we note that it is basically the quantity $((E(j)-E(i))/2V(ij))$ which induces the variation of the photoproduct quantum yield. In ammonia/methanol solution, only the bilirubin with the intrinsically different chromophores shows this variation. For the symmetric *BR*s in serum albumin it would seem that the above quantity for one of the originally identical chromophores has been changed by its binding to serum albumin. The appropriate asymptotic ratios for the two photoproduct quantum yields in ammonia/methanol solution are equal within experimental error; therefore, $p(\lambda)$ is constant or varies only little with wavelength within experimental error. The agreement between the asymptotic experimental photoproduct quantum yield ratio for *BR* IX$\alpha$ in serum albumin and the ratio as calculated from known values of $E(j)-E(i)$ and $V(ij)$ [3] also suggests that $p(\lambda)$ is constant or exhibits only small variation for this system.

We have recently shown [4] that the photoproduct quantum yield variations under discussion resemble more likely S-shaped curves than straight lines. Therefore, the straight line approach to data fitting, as done in Ref. [1], should be replaced by our asymptotic approach.

## Acknowledgements

We are grateful to Prof. *Giulio Iori*, Department of Biology, University of Padova, Padova, Italy, for helpful discussions.

## References

[1] McDonagh AF, Agati G, Lightner DA (1998) Monatsh Chem **129**: 649

[2] Harada N, Nakanishi K (1983) Circular Dichroic Spectroscopy. University Science Books, Oxford, UK

[3] Troup GJ, Agati G, Fusi F, Pratesi G (1996) Aust J Phys **49**: 673

[4] Troup GJ, Deakin MAB, Agati G, Fusi F, Pratesi R (1999) 8th ESP Congress (Granada, Spain), Abstract P126

*Received November 29, 1999. Accepted December 13, 1999*