Fluorescence Spectra and Singlet Energy of Conjugated Dienes

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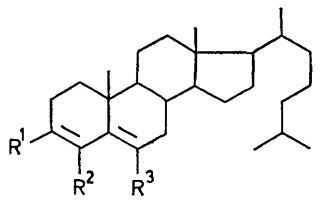
Summary Fluorescence spectra of seven cholestadienes have been recorded and their singlet energies have been determined.

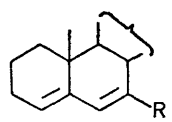
BUTA-1,3-DIENE and alkyl substituted acyclic derivatives exhibit no fluorescence (or phosphorescence) emission, and, among cyclic dienes, only ergosterol is reported to fluoresce.[1] We have found that the cholestadienes (**1**)—(**7**) exhibit fluorescence emission and we have recorded their spectra.

The spectra are not well resolved, and so we had to choose the onset of the curve as the $0 \rightarrow 0$ transition band. Using this approximation, we determined the ES^1 (singlet energy) values in the Table.

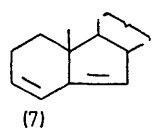
The ES^1 values of these *s-trans*-dienes are all *ca.* 90 kcal/mol and are lower than those obtained by other methods for buta-1,3-diene: 100—125 kcal/mol[2,3] and also lower than that for ergosterol (95 kcal/mol) which has an *s-cis*-diene chromophore. The change in ES^1 values for dienes (**1**)—(**4**), which differ by one methyl group, are too small to be of significance and are anyway within experimental errors, mainly because of our approximations. It is known that a rigid conjugated enone[4] and several cholestenones[5] exhibit phosphorescence[3] whereas the same chromophore borne on a more flexible



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = Me; R^2 = R^3 = H$
(3) $R^1 = R^3 = H; R^2 = Me$
(4) $R^1 = R^2 = H; R^3 = Me$



(5) R = H
(6) R = Me



(7)

TABLE

	Absorption	Emission[a]			
	λ_{max}/nm (ϵ)	c/mol l^{-1} [b]	λ_{max}/nm	$\lambda(0\rightarrow0)$/nm	ES^1/kcal mol^{-1}
(**1**)	235 (18,000)	5×10^{-3}	334	312	91·5
(**2**)	239 (19,500)	$1{\cdot}35 \times 10^{-3}$	342	314	91
(**3**)	238 (20,000)	6×10^{-3}	370	314	91
(**4**)	242 (20,000)	$1{\cdot}2 \times 10^{-3}$	430	313	91
(**5**)	238 (20,300)	4×10^{-4}	330	316	90·5
(**6**)	243 (20,500)	$2{\cdot}5 \times 10^{-3}$	435	326	88
(**7**)	250 (15,800)	1×10^{-2}	329	310	92·5

[a] The spectra are recorded either with a PMQII Zeiss or a FICA 55,000 spectrofluorimeter; the spectra of (**1**), (**2**), (**6**), and (**7**) have been recorded with both. [b] The cyclohexane solutions have such a concentration that the optical density is 0·3 for all dienes excited at the same wavelength: 300 nm.

skeleton does not. Beside ergosterol, the cholestadienes (**1**)—(**7**) provide another striking example of deactivation by light emission which, in such rigid molecules, is faster than vibrational relaxation.

We thank Dr. N. Ivanoff, and J. F. Delouis, Université Paris-Sud Orsay for discussions and technical assistance.

(*Received, 13th February* 1974; *Com.* 199.)

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