charide derivatives with lysozyme have shown that complexes of short oligosaccharides need not be completely analogous to that of, say, $(\mathrm{GlcNAc})_3$.[21] GlcNAc-β(1→4)-xylose, for instance,[21] is bound in the region C–D, but makes somewhat different contacts than predicted[3] for a productive complex of a GlcNAc polymer.

There can now be no doubt as to the correctness of Phillips' hypothesis that there is steric hindrance to a hydroxymethyl group at C-5 in a pyranose unit bound in subsite D of lysozyme.[3,4] Estimates of the "strain" (unfavorable interaction) range from 4 to 8 kcal/mol.[4,7,18,22,23] The important question which remains is how much such strain contributes to the lowering of the activation energy for cleavage of the glycosidic bond; we hope to approach this problem by studying the enzymic cleavage of glycosides of the XylNAc derivatives reported above.

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Near Unit Efficiency of Triplet Production in an Electron-Transfer Reaction

Sir:

Recent reports from this laboratory have indicated the required intermediacy of fluoranthene (FA), and possibly 10-methylphenothiazine (10-MP), triplet states in the chemiluminescent oxidation of the fluoranthene anion radical by the 10-MP cation radical in *N*,*N*-dimethylformamide (DMF)[1–3]

$$\mathrm{FA}^{\cdot -} + \text{10-MP}^{\cdot +} \longrightarrow {}^{3}\mathrm{FA}^{*} + \text{10-MP} \tag{1}$$

and possibly

$$\mathrm{FA}^{\cdot -} + \text{10-MP}^{\cdot +} \longrightarrow \mathrm{FA} + {}^{3}\text{10-MP}^{*} \tag{2}$$

It has also been shown that these triplet states can be intercepted by suitable electrochemically inert triplet energy acceptors, such as anthracene, pyrene, and *trans*-stilbene. In fact, we have utilized this property in a determination of the overall triplet yield of (1) and (2), wherein *trans*-stilbene served as an interceptor and the yield could be calculated from the amount of *cis*-stilbene produced by a known number of charge-transfer events.[2]

Our first such measurements indicated a triplet yield of 0.7% for electron transfer in the fluoranthene–10-MP system.[2] Though we initially accepted this value as characteristic of (1) and (2), recent absolute luminescence measurements carried out in this laboratory by Bezman[3] have led us to reexamine the meaning of this early result. In particular, the absolute measurements suggest a strong inverse dependence of the triplet yield on the concentration of 10-MP used as a substrate. Such behavior is apparently indicative of redox pathways other than (1) and (2) which compete for fluoranthene anion, and it has been ascribed tentatively to the presence of the dimer cation equilibrium[4–6]

$$\text{10-MP}^{\cdot +} + \text{10-MP} \rightleftharpoons (\text{10-MP})_2{}^{\cdot +} \tag{3}$$

Since several thermodynamic and structural arguments support the idea that the redox reaction involving the dimer cation is incapable of efficient product excitation,[3] one expects the measured triplet yield to decline with concentration of 10-MP, as the dimer cation participates in a progressively larger share of redox events. Bezman's data corroborate the 0.7% triplet yield at 20 m*M* 10-MP (at which the interception measurements were executed), but they indicate quite a high yield for the primary excitation process, (1) and (2). A rough estimate is about 30%.

In a continuing examination of these hypotheses, we have carried out several experiments in which the 10-phenylphenothiazine (10-PP) cation has been substituted for 10-MP$^+$. Because the dimer cations apparently exist in sandwich configurations with a 3–4-Å spacing between moieties,[6] it was felt that the phenyl substitution might sterically hinder the aggregation of 10-PP$^{\cdot +}$ and that higher triplet yields might be observed at the 20 m*M* concentration levels at which interception measurements can be made most conveniently.[7]

Preliminary investigations showed 10-PP to have all the requisite electrochemical and spectroscopic properties; indeed, its behavior is essentially identical with that of 10-MP (Table I).[1] Figure 1 displays the chemiluminescence spectrum obtained from the 10-PP–fluoranthene system. At short wavelengths, the emission distribution is very similar to the fluorescence of

Table I. Electrochemical and Spectroscopic Data

Compound	$E_p(\mathrm{R/R}^{\cdot +})$[a]	$E_p(\mathrm{R/R}^{\cdot -})$[a]	Lowest triplet, eV	First excited singlet, eV
Fluoranthene	NO[b]	−1.70	2.3	3.0
10-MP	0.90	NR[c]	(2.4)[d]	3.0
10-PP	0.88	NR[c]	(2.4)[d]	3.0

[a] Cyclic voltammetric peak potentials, in volts *vs.* Ag|AgCl, KCl (saturated), for reversible waves at a Pt disk in DMF with 0.1 *M* tetra-*n*-butylammonium perchlorate. Scan rate = 0.2 V/sec. [b] NO = not oxidized before anodic background limit (+1.3 V). [c] NR = not reduced before cathodic background limit (−2.6 V). [d] Value for phenothiazine from J. M. Lhoste and J. B. Merceille, *J. Chim. Phys. Physicochim. Biol.*, **65**, 1889 (1968).

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either fluoranthene or 10-PP, but the long wavelength region of the chemiluminescence is markedly enhanced in comparison to either fluorescence distribution. This latter portion of the chemiluminescence spectrum suggests a second, lower energy emitter, which may be an excimer or exciplex, or even a triplet state. In any case, all emission is totally quenched by *trans*-stilbene, so both emissions probably arise through common triplet intermediates. In addition, in a manner similar to that for the fluoranthene–10-MP system, the addition of anthracene also quenches the normal chemiluminescence, producing instead the characteristic anthracene emission. This behavior has been shown previously to be characteristic of systems involving triplet intermediates and, in conjunction with the fact that the electron-transfer reaction enthalpy is insufficient to raise either fluoranthene or 10-PP to its first excited singlet state, points to the fluoranthene–10-PP system as a typical energy-deficient system yielding emission by the T route.[1]

Table II lists the triplet yields obtained with this system in DMF. The experimental methods were essentially as described previously,[2] with the exception that a smaller cell (22 *vs.* 50 ml) was used. The results show that triplet production is considerably enhanced in this case as compared to the fluoranthene–10-MP system and that the yield is not a significant function of concentration.

Table II. Triplet Yields and Pertinent Experimental Data

Initial concentrations, m*M*[a] 10-PP	Fluoranthene	*trans*-Stilbene	Electrolysis time[c]	Charge passed, *Q*, C	Cis/trans[b]	Triplet yield
9.4	19.7	19.6	69	54.8	1.57	0.79
10.9	18.7	22.2	47	57.9	1.29	0.78
21.3	32.4	28.1	51	74.0	1.46	0.81
20.0	41.5	62.5	49	74.0	0.38	0.82

[a] Each solution contained 0.1 *M* tetrabutylammonium tetrafluoroborate as supporting electrolyte. [b] For electrolyzed solution. Gas chromatographic analysis showed that the final concentration of *cis*- plus *trans*-stilbene was equal to the initial concentration of *trans*-stilbene within ±2%. [c] In minutes.

In considering the triplet yields of Table II, it is important to recognize an uncertainty resulting from the unknown isomerization efficiency, ϕ_{tc}, accompanying triplet quenching in DMF, *e.g.*

$$^3FA^* + trans\text{-stilbene} \longrightarrow FA + \phi_{tc}(cis\text{-stilbene}) + (1 - \phi_{tc})(trans\text{-stilbene}) \quad (4)$$

Hammond and his coworkers have shown that triplet stilbene decays to the cis isomer with 59% efficiency,[8] but a recent study has indicated less than unit efficiency for triplet energy transfer in quenching by *trans*-stilbene,[9] so that the overall isomerization yield ϕ_{tc} can sometimes be lower than 0.59. In the absence of direct measurements of the effective ϕ_{tc} for the system at hand, we have taken 0.59 as the value for computations involved in Table II. Thus one can consider the triplet yields displayed there as lower limits, unless an unanticipated solvent effect raises the triplet stilbene partition efficiency above 0.59. Obviously it is quite possible that ϕ_{tc} could be as low as 0.47 and that the triplet yields could be as high as unity.

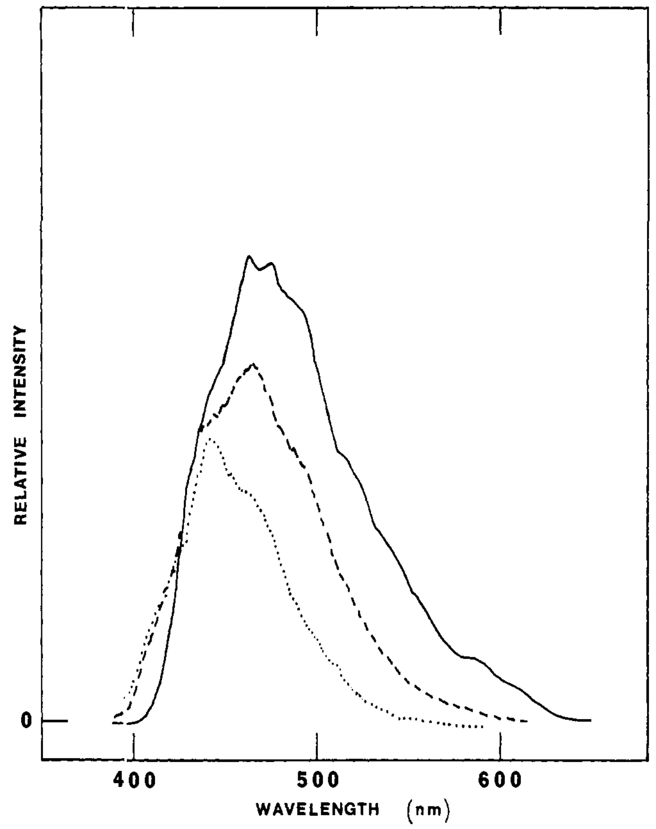

Figure 1. Chemiluminescence and fluorescence emission spectra from DMF solutions. Solid curve: chemiluminescence spectrum from the fluoranthene anion–10-PP cation reaction in DMF; generating electrode cycled at 20 Hz between +0.90 and −1.80 V *vs.* Ag|AgCl; KCl (saturated); fluoranthene and 10-PP concentrations were 1 m*M*. Dashed curve: fluoranthene fluorescence, 10^{-5} *M*. Dotted curve: 10-PP fluorescence, 10^{-5} *M*.

Apart from the uncertainty resulting from the unknown isomerization efficiency, one other factor, that of possible triplet interception by *cis*-stilbene, must be considered. Because this process causes partial reversion of *cis*-stilbene back to the trans form, one could obviously require a significant upward correction in the triplet yields if such quenching were competitive with triplet interception by *trans*-stilbene. However, two observations militate against this possibility. First, it is observed that chemiluminescence from the present system is not strongly quenched even in the presence of a large excess of *cis*-stilbene, thereby indicating that *cis*-stilbene is a much poorer quencher of the triplet intermediates than the trans form in DMF. Moreover, the data of Table II show that even though the initial *trans*-stilbene concentration is varied over a wide range, the amount of *cis*-stilbene produced per charge-transfer event remains quite insensitive to the variation. Calculations from the integrated rate law for *cis*-stilbene production suggest that this behavior would be expected if the rate of triplet interception by the cis isomer were small compared to the *trans*-stilbene interception rate. In the absence of accurate rate constants for these energy-transfer processes, our triplet yields must stand uncorrected, but the observations above suggest that the corrections, if any, are quite small.

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In any circumstance, the yields are surely quite large and they seem to be independent of 10-PP concentration; thus the present results support the dimer cation equilibrium as an effective means for lowering the triplet generation efficiencies in susceptible systems. Moreover, they reinforce most directly the hypothesis, advanced earlier, that initial excitation frequently is very efficient in these systems and that low luminescence yields often result from inefficiencies subsequent to electron transfer.

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X-Ray Crystallographic and Solution Nuclear Magnetic Resonance Studies of 1,3,5,7-Tetrathiocane

Sir:

Nmr results on 1,3,5,7-tetrathiocane $(CH_2S)_4$, described below, suggest that this cyclic tetramer of thioformaldehyde does not exhibit the crown conformation commonly found in analogous heterocyclic eight-membered ring compounds. Unit cell parameters have been reported for crystalline $(CH_2S)_4$,[1] and the space group was reported to be $P2_1/c$, with three crystallographically nonequivalent molecules in the asymmetric unit. We have determined the crystal structure of this compound with X-ray diffractometer data. The unit cell parameters, $a = 20.27$, $b = 8.73$, and $c = 13.44$ Å, $\beta = 99.72°$, are essentially the same as those previously reported.[1]

X-Ray crystallographic data were collected with a Syntex $P\bar{1}$ automated diffractometer, with graphite monochromatized Mo $K\alpha$ radiation. The reflection intensities were measured from a crystal of cuboidal shape having average linear dimensions of 0.2 mm. All independent reflections were measured out to a value of $(\sin\theta)/\lambda = 0.6$ Å^{-1}. Standard reflections were observed to decrease in intensity in an approximately linear fashion during data collection, and this was ascribed to crystal decomposition and sublimation. The intensities were corrected for this fall-off, which amounted at most to 25%. In all, 1783 reflections were taken to be observable.

Values of $|E|_{hkl}$ as customarily defined were calculated for all reflections by the application of Wilson[2] statistics. Signs for all E values of magnitude greater than 1.7, about 400 in all, were determined by application of Sayre's relation[3] in the computer program of Long.[4] A three-dimensional E map then revealed 12 peaks of about the same height, at least twice as high as any other peaks observed. These were taken to be the 12 independent sulfur atoms, and the positions were used to calculate a set of signs. All carbon atom positions were then determined by two iterations of difference electron density maps. Refinement of the atomic positions by full-matrix least-squares methods[5] with anisotropic temperature parameters converged with an R value of 0.092.

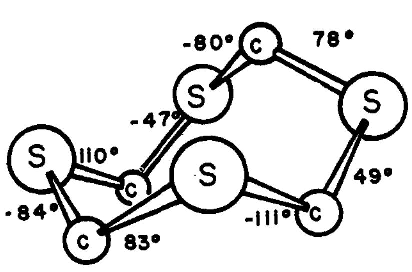

Figure 1. 1,3,5,7-Tetrathiocane molecule in the boat–chair conformation. Torsion angles are indicated about each bond.

At the present stage of refinement, the esd's for sulfur and carbon atom positions are 0.006 and 0.02 Å, respectively. Within limits of error, the three crystallographically nonequivalent molecules exhibit the identical boat–chair conformation, illustrated in Figure 1. The molecular geometry averaged overall gives the following values: S–C bond length = 1.82 Å, S–C–S bond angle = 116°, and C–S–C bond angle = 103°, with no significant deviations from these values. The torsion angles shown in Figure 1 for successive bonds are averaged over the three molecules, whose respective values do not in any case differ significantly. Atomic positions are given in Table I.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the Atoms in the Three Crystallography Independent Molecules in the Structure of 1,3,5,7-Tetrathiocane[a]

Atom	x	y	z	B
S(1a)	0.016	0.204	0.439	3.1
S(2a)	−0.015	0.152	0.206	3.1
S(3a)	0.135	0.176	0.199	3.2
S(4a)	0.166	0.215	0.432	3.2
C(1a)	−0.031	0.095	0.331	2.7
C(2a)	0.063	0.055	0.197	2.1
C(3a)	0.135	0.294	0.309	2.5
C(4a)	0.095	0.105	0.460	1.9
S(1b)	0.306	0.243	0.251	2.8
S(2b)	0.342	0.177	0.040	2.9
S(3b)	0.492	0.150	0.139	3.4
S(4b)	0.455	0.220	0.346	3.8
C(1b)	0.307	0.106	0.147	2.3
C(2b)	0.419	0.069	0.056	2.2
C(3b)	0.478	0.074	0.260	3.0
C(4b)	0.389	0.328	0.270	2.0
S(1c)	0.662	0.283	0.141	3.2
S(2c)	0.653	0.320	−0.092	3.0
S(3c)	0.805	0.265	−0.068	3.4
S(4c)	0.814	0.235	0.163	3.6
C(1c)	0.630	0.387	0.025	3.8
C(2c)	0.740	0.403	−0.090	2.6
C(3c)	0.792	0.147	0.041	2.4
C(4c)	0.745	0.366	0.173	2.3

[a] a, b, and c in parentheses refer to the different rings.

The 251-MHz proton spectrum of 1,3,5,7-tetrathiocane in $CHCl_2F$ is a sharp singlet at room temperature (τ 5.95) and remains unchanged down to −170°. In contrast, the proton spectrum of the related 1,3,5,7-tetroxocane, $(CH_2O)_4$, shows the presence of two con-

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