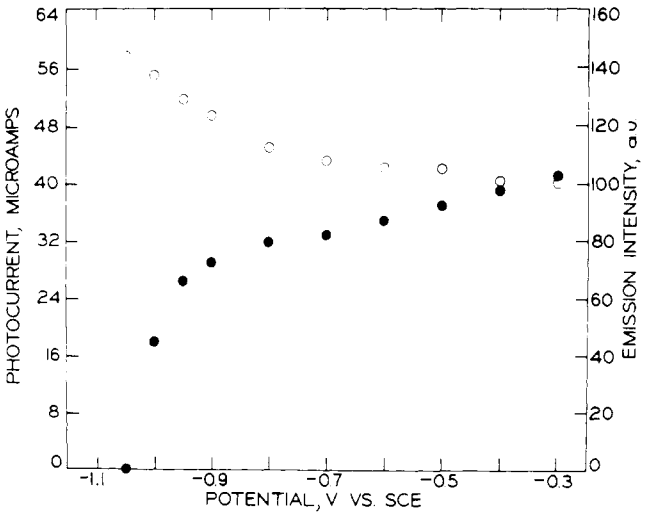

Figure 1. Emission intensity (right-hand scale and O) monitored at 600 nm and photocurrent (left-hand scale and ●) for a 5-ppm CdS:Te-based PEC employing unstirred 1 M OH^-/1 M S^{2-}/0.2 M S electrolyte. The polysulfide electrolyte redox potential is at −0.72 V vs. SCE so that optical to electrical energy conversion obtains at voltages more negative than this value. The 10 × 10 × 3 mm photoelectrode was excited with 5 mW in an ~3-mm-diameter beam (~70 mW/cm^2) of 488-nm light; this intensity has been corrected for solution absorbance. Quantum yields for electron flow in the external circuit may be determined by dividing the photocurrent values by 2000.

yields similar intensity increases, generally 20–80%. However, emission from irradiation at 514.5 nm on the band gap edge is expected and observed to be less sensitive to electrode potential, since a much smaller fraction of incident light is absorbed within the depletion region.[18] Under the conditions of Figure 1, excitation at 514.5 nm yields substantially reduced photocurrents and <6% variation in the emission intensity over the same potential range. As with other PECs, optical to electrical energy conversion occurs at potentials more negative than ~−0.7 V vs. SCE, the polysulfide redox potential.[1,2]

Although it is intriguing to speculate that radiative deactivation might increase directly at the expense of the nonradiative deactivation route represented by photocurrent, a complete energy balance including the predominant nonelectrochemical, nonradiative decay route is required to determine the extent to which such a trade-off occurs. We estimate the best optical to electrical conversion efficiencies to be ~0.6%, corresponding to an output voltage of 0.23 V and a quantum efficiency for electron flow in the external circuit of 0.06 from an input power of 1.3 mW (18.2 mW/cm^2) at 488.0 nm. A reasonable upper limit of emission quantum efficiency is 0.025, based on our observation that the 77 K CdS:Te emission spectrum is ~40 times the 298 K intensity. Measurements with a flat-response radiometer of the back surface emission off CdS:Te electrodes indicate that conversion to emission can be as large as 0.1–1.0%. We should point out that the efficiencies reported here for CdS:Te-based PECs have not been optimized and that several other PEC parameters including electrolyte and temperature can be expected to influence efficiency. A detailed characterization of the CdS:Te-based PEC is in progress and will be reported in the full paper.

Note Added in Proof. The use of Br_2/MeOH as an etchant results in substantially improved optical to electrical energy conversion efficiencies of 3–5% with 500-nm excitation. The luminescent properties described above are preserved with this etchant.

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(15) Samples were obtained from Eagle-Picher Industries, Inc., and had resistivities of ~1 Ω-cm (Hall method). The material was used in irregular shapes, generally 0.5–1.0 cm^2 in surface area and 0.1–0.8 cm thick. We find variations in PEC properties within and between samples that are nominally doped at the same Te concentration, so that doping levels must be considered approximate. Local variations are also a consequence of grain boundaries.
(16) Starting weight, 1.9750 g; final weight, 1.9749 g. CdS:Te (100 ppm) was photolyzed with a UV-filtered 200-W Hg lamp for 210 h at an average photocurrent of 0.066 mA in 1 M OH^-/1 M S^{2-}/0.2 M S at −0.05 V vs. a Pt counterelectrode. The expected weight loss (eq 1) is 0.0373 g.
(17) We have avoided both the use of CdS:Te as a cathode and extreme voltages which can decompose the electrode electrochemically. See A. J. Bard and M. S. Wrighton, *J. Electrochem. Soc.*, **124**, 1706 (1977), and H. Gerischer, *J. Electroanal. Chem.*, **82**, 133 (1977).
(18) We estimate the absorptivity of the CdS:Te samples to be ~10^3 cm^{-1} at 514.5 nm and ~10^4–10^5 cm^{-1} for ultraband gap wavelengths based on data in ref 13a,c and 14, and our own relative transmission measurements at these wavelengths; the depletion region is estimated to be 10^{-4}–10^{-5} cm thick.

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Potential Proximate Carcinogens of 7,12-Dimethylbenz[*a*]anthracene: Characterization of Two Metabolically Formed *trans*-3,4-Dihydrodiols

Sir:

7,12-Dimethylbenz[*a*]anthracene (**1**) is one of the most potent carcinogenic polycyclic aromatic hydrocarbons known, and is much more potent than the more extensively studied carcinogen, benzo[*a*]pyrene.[1,2] Metabolic activation by mammalian drug-metabolizing enzyme systems is required for the biological properties exhibited by **1**.[2] Enzymatic hydroxylation at the 7-methyl group yields 7-hydroxymethyl-12-methylbenz[*a*]anthracene (**2**) which has higher adrenocorticolytic activity[3] and has similar or reduced carcinogenicity[3,4] in comparison with those of **1**. It has been suggested[5]

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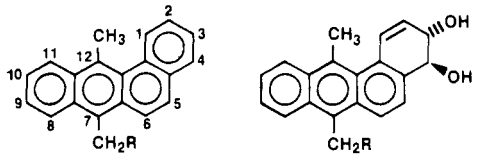

1, R = H 3, R = H
2, R = OH 4, R = OH

that oxidative metabolism at the 1,2,3,4 ring of **1** is responsible for the formation of a reactive carcinogenic metabolite, presumably the bay-region[6] 3,4-diol 1,2-epoxide. Structurally similar bay-region diol epoxides and their dihydrodiol precursors have been shown to be generated metabolically from benzo[*a*]pyrene,[7] 3-methylcholanthrene,[8] 5-methylchrysene,[9] and 7-methylbenz[*a*]anthracene.[10] We report the detailed characterization of two optically active *trans*-3,4-dihydrodiol metabolites (**3** and **4**) which have not hitherto been reported as metabolites of **1** either in vivo or in vitro. These two *trans*-3,4-dihydrodiols have greater in vitro DNA binding and mutagenic activities than their parent hydrocarbons upon further metabolism and therefore are potential proximate carcinogenic metabolites.

For the purpose of structural elucidation, the metabolites were obtained by in vitro incubation of 0.08 mmol of **1** with rat liver microsomes from 50 g of wet livers and a NADPH-generating system in a 1-L reaction mixture at 37 °C for 1 h. Liver microsomes were prepared from phenobarbital-pretreated (75 mg/kg of body weight for 3 days) male Sprague-Dawley rats weighing 80–100 g. Under the incubation conditions, ~60% of the substrates were metabolized. Substrate and metabolites were extracted with 3 L of 2:1 ethyl acetate–acetone and were subsequently isolated by semipreparative LC.[11] The methylhydroxylated derivative **2** and *trans*-3,4-dihydrodiols **3** and **4** were among the many major metabolites formed from **1**.[11] *trans*-3,4-Dihydrodiol **4** was found to be the most abundant metabolite from the in vitro incubation of **2**.[11] All dihydrodiol formations were completely abolished when the incubation mixture included 1 mM of the epoxide hydratase inhibitor 3,3,3-trichloropropylene oxide.

Ultraviolet absorption spectra[12] of optically active[13] **3** and **4** were compared those of the five synthetic standards, benz[*a*]anthracene *trans*-1,2-dihydrodiol and its 3,4, 5,6, 8,9, and 10,11 isomers,[14a] confirming that they are saturated at the 3 and 4 positions. Mass spectral analysis of **3** and **4** confirmed that the molecular weights are 290 and 306, respectively.[15] The ^{1}H NMR spectra (200 MHz, $CDCl_3$; $CHCl_3$ at δ 7.25 as internal standard)[16] allowed assignments as *trans*-3,4-dihydrodiols. **3:** δ 7.07 (dd, 1, H_1), 6.15 (dd, 1, H_2), 4.73 (br d, 1, H_3), 4.83 (d, 1, H_4), 7.73 (d, 1, H_5), 8.16–8.35 (m, 3, $H_{6,8,11}$), 3.08 (s, 3, 7-CH_3), 7.46–7.60 (m, 2, $H_{9,10}$), and 3.14 (s, 3, 12-CH_3) ppm with $J_{1,2}$ = 10.7, $J_{2,3}$ = 2.0, $J_{3,4}$ = 11.9, $J_{1,3}$ = 1.8, and $J_{5,6}$ = 9.1 Hz. **4:** δ 7.06 (dd, 1, H_1), 6.19 (dd, 1, H_2), 4.76 (br d, 1, H_3), 4.90 (d, 1 H_4), 7.80 (dd, 1, H_5), 8.37–8.47 (m, 2, $H_{6,8}$), 5.65 (s, 2, 7-CH_2), 7.51–7.65 (m, 2, $H_{9,10}$), 8.29 (m, 1, H_{11}), and 3.18 (s, 3, 12-CH_3) ppm with $J_{1,2}$ = 10.7, $J_{2,3}$ = 2.1, $J_{1,3}$ = 2.0, $J_{3,4}$ = 11.6, and $J_{5,6}$ = 9.1 Hz. The trans configurations are assigned on the basis of the relatively large coupling constants $J_{3,4}$, whereas much smaller coupling constants are expected for the cis configuration.[17] The olefinic double bonds at the C_1 and C_2 are clearly indicated by the chemical shifts of H_1 and H_2 and the large coupling constants $J_{1,2}$.[17] Two aromatic protons H_6 and H_8 are shifted downfield from δ 8.27 (multiplet center) in **3** to 8.41 (multiplet center) in **4**. The proton singlet of 7-CH_3 in **3** is absent in **4** and the proton singlet of 7-CH_2 is at δ 5.65 in **4**. In contrast to the benzylic vinyl hydrogens of *trans*-3,4-dihydroxy-3,4-dihydrobenz[*a*]anthracene[14a] and *trans*-9,10-dihydroxy-9,10-dihydro-1-hydroxy-3-methylcholanthrene,[6] the chemical shifts of H_1 in **3** and **4** do not overlap with other aromatic hydrogens and occur at relatively higher field presumably owing to lesser conjugation of 1,2 double bond with anthracene nucleus.[18] Mass spectral analyses of **3** and **4**, which were treated in anhydrous acetone in the presence of catalytic amount of anhydrous $CuSO_4$ (2 h at room temperature), failed to show the formation of vicinal cis acetonide.[19] This provides further evidence that H_3 and H_4 are in trans configuration.

Recent results indicate that **3** and **4** bind to DNA substantially more than **1** and **2**, respectively, upon further metabolic activation in an in vitro microsomal enzyme system.[20a] Furthermore, **3** and **4** are 8-fold and 20-fold more mutagenic than **1** and **2**, respectively, toward Chinese hamster V79 cells in a mammalian cell mediated mutagenicity assay.[20b,21] All other dihydrodiol metabolites of **1** and **2** that have been tested are of much lower mutagenic activity.[20b,21] These findings suggest that **3** and **4**, whose structural characterizations have been reported herein, may be proximate carcinogenic metabolites. Further metabolism of two other known metabolites, 7-methyl-12-hydroxymethylbenz[*a*]anthracene and 7,12-dihydroxymethylbenz[*a*]anthracene,[3] to the reactive 3,4-diol 1,2-epoxides is also possible.[20a] These results indicate that there are multiple activation pathways which contribute to the biological properties of the potent carcinogen 7,12-dimethylbenz[*a*]anthracene.

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(12) The diagnostic ultraviolet absorption maxima in nanometers and their extinction coefficients (cm^{-1} M^{-1}, shown in parenthesis) follow: **3**, 432.0 (10 200), 407.3 (10 600), 386.1 (5900), 271.2 (143 000); **4**, 428.2 (10 800), 404.1 (11 300), 383.1 (6200), 270.1 (159 000). Ultraviolet absorption spectra were measured in methanol on a Cary 118C spectrophotometer. For the determination of extinction coefficients, **3** (or **4**) was obtained from ^{14}C-labeled **1** (or **2**) of known specific activity.

(13) The optical rotations were measured on a Perkin-Elmer 241-MC polarimeter with a cell of 2-cm light path length: **3**, $[\alpha]^{25}_D$ −174° (0.32 mg/mL, methanol); **4**, $[\alpha]^{25}_D$ −138° (0.65 mg/mL, methanol). Although **3** and **4** are optically active and may each be a single enantiomer, the structures shown for **3** and **4** do not imply absolute stereochemistry.

(14) (a) For ultraviolet absorption spectra and NMR spectra of benz[*a*]anthracene *trans*-dihydrodiols, see R. E. Lehr, M. Schafer-Ridder, and D. M. Jerina, *J. Org. Chem.*, **42**, 736–744 (1977); (b) D. M. Jerina, H. Selander, H. Yagi, M. C. Wells, J. F. Davey, V. Mahadevan, and D. T. Gibson, *J. Am. Chem.*

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(15) Mass spectral analysis was performed on a Finnigan 4000 GC/MS/Data System by electron impact with a solid probe at 70 eV and at 250 °C ion source temperature. The diagnostic ions (with relative ion intensities shown in parenthesis) follow: **3** (at 185 °C probe temperature), *m/e* 290 (M^+, 100%), 275 (13), 272 (22), 257 (25), 244 (84), 229 (73), 215 (65), 202 (88), 189 (30); **4** (at 210 °C probe temperature), *m/e* 306 (M^+, 67%), 291 (5), 288 (26), 260 (38), 244 (43), 231 (59), 216 (83), 215 (100), 202 (89), 189 (37).
(16) NMR spectral analysis was performed on a Varian Model XL-200 NMR spectrometer at 24 °C. We thank Dr. George Gray of Varian Associates, Inc., for obtaining the NMR spectra.
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(18) The bathochromic shifts of UV absorption maxima of **1**, **2**, **3**, and **4** relative to UV absorption maxima of benz[*a*]anthracene and benz[*a*]anthracene *trans*-3,4-dihydrodiol are apparently due to the presence of 7-CH_3 (or 7-CH_2OH) and the steric strain between the 12-CH_3 and H_1: M. A. Frisch, C. Barker, J. L. Margrave, and M. S. Newman, *J. Am. Chem. Soc.*, **85**, 2356–2357 (1963). Presumably the steric strain decreased the conjugation of 1,2 double bonds with anthracene nucleus in **3** and **4** compared with the 1,2 double bonds of *trans*-3,4-dihydroxy-3,4-dihydrobenz[*a*]anthracene and *trans*-9,10-dihydroxy-9,10-dihydro-1-hydroxy-3-methylcholanthrene and consequently the H_1 of **3** and **4** occurs at higher field. **1** is a nonplanar molecular with 1,2,3,4 ring inclined to that of anthracene nucleus at an angle of 18.5°: J. Iball, *Nature (London)*, **201**, 916–917 (1964).
(19) Under identical conditions, the *cis*-5,6-dihydrodiol of **1** yielded vicinal cis acetonide (M^+ at *m/e* 330) quantitatively.
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(21) Since the submission of this manuscript, C. Malaveille et al. (*Biochem. Biophys. Res. Commun.*, **83**, 1468–1473 (1978)) reported high mutagenic activity of a chemically synthesized **3** (presumably the racemic trans isomer) toward *S. typhimurium* test strain TA100 in a rat liver microsome mediated mutagenicity assay.

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New Model Visual Pigments. Spectroscopy of Poly(ethylene glycol) Peptide Schiff Bases of Retinal

Sir:

Considerable knowledge is currently available[1-3] regarding the spectral and photochemical properties of various model visual pigment systems including retinals, retinols, and retinyl Schiff bases (RSB). However, as far as the understanding of the visual process itself is concerned, there are still many unresolved questions. Some of these concern the origin of the long-wavelength absorption maxima[4-6] of rhodopsin, the high photoisomerization quantum yield[7] of rhodopsin (both compared with protonated 11-cis RSB), and the mechanism of the primary photoprocesses.[8-10] Obviously, the environmental effect of the protein envelope and other internal interactions such as charge transfer and hydrogen bonding need to be investigated via models that more accurately mimic rhodopsin.

We have undertaken the spectroscopic study of a series of RSB complexes of poly(ethylene glycol) (PEG) amino acids and oligopeptides with selected amino acid sequencing. The absorption and emission spectral data for these systems under various conditions of solvents, cations, proton donors, and charge transfer agents will appear in the full paper. In this communication we report briefly the results for the all-trans

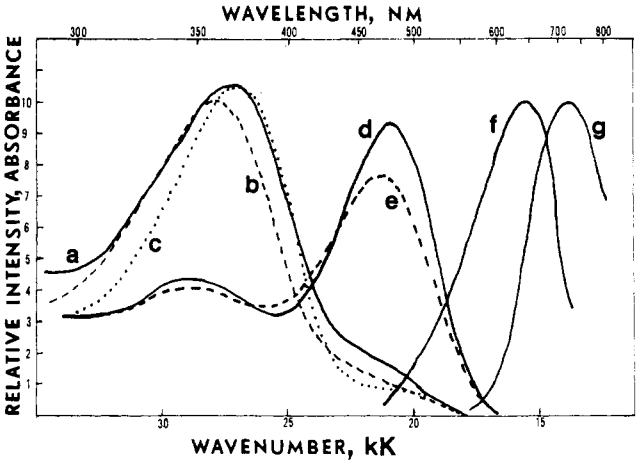

Figure 1. Absorption, emission, and excitation spectra of RSB of PEG-Ala-Lys-Glu in dichloromethane: (a) —, absorption spectrum of RSB at 193 K; (b) - - -, absorption spectrum of RSB at 298 K; (c) . . . , excitation spectrum of RSB at 193 K (monitored at 570 nm); (d) —, absorption spectrum of protonated RSB at 193 K; (e) - - -, absorption spectrum of protonated RSB at 298 K; (f) —, emission spectrum of RSB at 193 K (excited at 370 nm); (g) —, emission spectrum of protonated RSB at 193 K (excited at 470 nm).

RSB complexes of the italicized amino acids of PEG-*Ala* (I), PEG-Ala-Phe-*Lys* (II) (α-amino group of Lys protected by *tert*-butyl oxycarbonyl group), PEG-Ala-*Lys*-Glu (III) (ϵ-carboxylic group of Glu free), and PEG-Phe-*Lys*-Ala-Glu (IV) (ϵ-carboxylic group of Glu free), where Ala = alanine, Phe = phenylalanine, Lys = lysine, and Glu = glutamic acid. The PEG peptides were prepared using PEG of mol wt 6000 by the method of liquid-phase peptide syntheses described in detail elsewhere.[11]

At room temperature in EtOH–MeOH (4:1, v/v), the absorption spectra of all of the peptide RSB's are characterized by a broad band with maximum at 335–365 nm, which upon cooling to 77 K undergoes a red shift by 5–10 nm. On protonation with trichloroacetic acid (TCA) two bands develop, one at 330–340 nm and the other, more intense, at 440–450 nm. The latter band (long wavelength) undergoes a blue shift of 5–10 nm upon cooling to 77 K. Figure 1 shows the absorption spectra of an RSB complex of the peptide III, PEG-Ala-Lys-Glu, and its protonated form in dichloromethane at 298 and 193 K. It should be noted that the main absorption band of III is accompanied by a long-wavelength tail (430–520 nm) which upon cooling to 193 K increases in intensity by ~50% while the intensity at the band maximum increases by only ~9%. The spectral region of the increased absorption corresponds to the spectral region where the formally protonated RSB complex has its absorption maximum. Similar experiments done on all-trans RSB of peptide IV, PEG-Phe-Lys-Ala-Glu, in CH_2Cl_2–CHF_2Cl (1:1, v/v) at 298 and 173 K show that the long-wavelength tailing is present in both room- and low-temperature spectra, but to a much lesser extent.

Each of the RSB–peptide complexes exhibits a weak fluorescence ($\phi_F = 10^{-2}$–10^{-3}) at room temperature in EtOH–MeOH and CH_2Cl_2. The intensity of fluorescence becomes enhanced on cooling (ϕ_F = 0.1–0.2 in EtOH–MeOH at 77 K and ~0.02 in CH_2Cl_2 at 193 K). The protonated RSB's also fluoresce moderately strongly at low temperature ($\phi_F \sim 0.1$ in EtOH–MeOH at 77 K and ~0.01 in CH_2Cl_2 at 193 K). Both in EtOH–MeOH and CH_2Cl_2 at low temperature, the shape, position, and intensity of fluorescence of the RSB's of the peptides III and IV are found to show a marked dependence on the excitation wavelength. Thus, for the RSB of peptide III in CH_2Cl_2 at 193 K, as the excitation wavelength is changed from 350 nm to 430 nm, the emission maximum undergoes a red shift of ~1000 cm^{-1}; furthermore, the fluorescence spec-

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