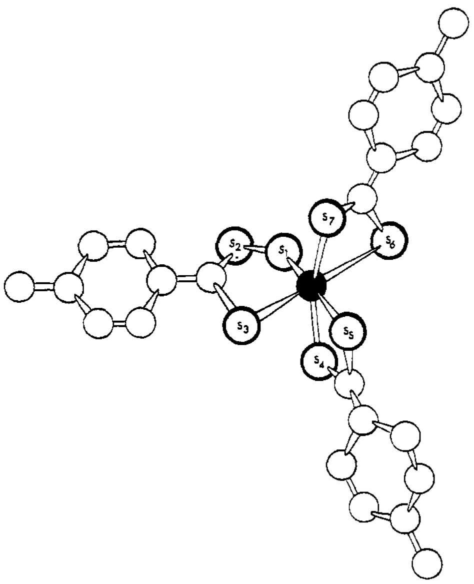

Figure 1. Molecular structure of Fe(TTD)(DTT)$_2$. The iron atom is at the center and carbon atoms are not labeled.

calculations.[8] At present the conventional R factor[9] for isotropic refinement of all atoms is 0.096 for 1225 observed reflections.

Table I. Selected Geometric Features of Fe(TTD)(DTT)$_2$[a,b]

Bond	Distance, Å	Interbond angle, deg	
Fe–S$_1$	2.19	S$_1$–Fe–S$_3$	92.8
Fe–S$_3$	2.23	S$_4$–Fe–S$_5$	73.9
Fe–S$_4$	2.29	S$_6$–Fe–S$_7$	73.8
Fe–S$_5$	2.33	S$_1$–S$_2$–C	111.7
Fe–S$_6$	2.35	S$_2$–C–S$_3$	121
Fe–S$_7$	2.31	S$_4$–C–S$_5$	113
S$_1$–S$_2$	2.09	S$_6$–C–S$_7$	110
Nonbonded			
Fe–S$_2$	3.44		
S$_1$–S$_3$	3.20		
S$_4$–S$_5$	2.78		
S$_6$–S$_7$	2.80		

[a] Bond distances reported have individual estimated standard deviations of ±0.02 Å and interbond angles of ±0.4° (S–Fe–S) and ±1° (S–C–S). [b] See Figure 1 for atom-labeling scheme.

The molecular structure of Fe(TTD)(DTT)$_2$ is shown in Figure 1. Selected bond lengths, angles, and other geometric features are summarized in Table I. The complex contains two four-membered chelate rings and one five-membered chelate ring, with six sulfur donor atoms coordinated to iron at the apices of a distorted octahedron. The geometry of the four-membered rings includes a mean Fe-S distance of 2.32 ± 0.02 Å, an average S-Fe-S angle of 73.8°, an average S-C-S angle of 111°, and an average "bite" distance of 2.79 ± 0.01 Å. These values are in general agreement with similar results obtained for other sulfur-coordinated iron complexes containing four-membered rings, Fe(NO)(S$_2$CN(CH$_3$)$_2$)$_2$[10] and FeCl(S$_2$CN(C$_2$H$_5$)$_2$)$_2$.[11] The geometric features of the five-membered ring are quite different, however, with an average Fe-S distance of 2.21 ± 0.02 Å, a S-Fe-S angle of 92.8°, a S-C-S angle of 121°, and a S···S bite of 3.20 Å. The values may be compared with the average Fe-S distance of 2.23 Å, S-Fe-S angle of 90°, and ligand bite distance of 3.15 Å recently found for $\{Fe(MNT)_2\}_2^{2-}$.[5,12] To a first approximation, therefore, the geometry of Fe(TTD)(DTT)$_2$ may be understood in terms of the "normal" constraints imposed by the participation of the iron atom in both four- and five-membered chelate rings with sulfur donor atoms, quite apart from any effect which the electronic structure of the ligand molecules might have. Other geometric features, *e.g.*, the near-planarity of the $CH_3C_6H_4CS_2$ groups and nonplanarity of the $CH_3C_6H_4CS_3$ ligand, may reflect the over-all electronic structure of the molecule as will be discussed in detail later.

The presence of Fe-S-S bonds in the present structure strongly supports the previous structural assignment for related "sulfur-rich" complexes of nickel[7] and zinc.[6] It also seems likely that such units occur in the more fully sulfurated iron complex mentioned above.

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[8] Programs for the IBM 7094 computer used in this work, in addition to various local programs written at the Brookhaven National Laboratory and kindly made available to us, were Burnham's GNABS absorption program, Zalkin's FORDAP Fourier program, and the Busing–Levy ORFLS least-squares program and ORFFE error function program.

[9] Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(10) M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Commun.*, 583 (1967); G. R. Davies, R. H. B. Mais, and P. G. Owston, *ibid.*, 81 (1968).

(11) B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211**, 627 (1966).

(12) W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967).

Synthesis of *all-trans*-5,6-Dihydroretinal, a New Visual Chromophore

Sir:

We wish to report the synthesis of 5,6-dihydroretinal,[1] a new synthetic visual chromophore. To our knowledge, *this is the only polyene aldehyde outside of retinal and 3-dehydroretinal that has ever been found to combine with a visual protein.* The starting point in the multistep synthesis was 2,2,6-trimethylcyclohexanone (I) which itself was obtained from 2-carbethoxycyclohexanone.[2] Grignard reaction of I with chloromethyl ethyl ether followed by hydrolysis with 98% formic acid afforded[3] dihydrocyclocitral (II) in moderate over-all yield: bp 45–47° (0.5 mm); ir (neat): 2718 (ν_{CHO}), 1718 ($\nu_{C=O}$), 1450 ($\delta_{as\text{-}CH_3}$), and 1380 cm^{-1} ($\delta_{s\text{-}gem\text{-}CH_3}$); mass spectrum, molecular ion at m/e 154; nmr: 1 H, doublet at τ 0.36 (J = 4 cps), 1 H, multiplet centered at 7.64, 1 H, multiplet centered at 8.09, 6 H, multiplet at 8.24–8.84, 3 H, singlet at 8.99, 6 H, closely spaced doublets at 9.02–9.10. Following a general procedure,[4]

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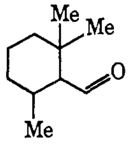
(1) The name 5,6-dihydroretinal is adopted for this compound according to the IUPAC nomenclature for carotenoids. The systematic name for this compound is 9-(2,2,6-trimethylcyclohexyl)-3,7-dimethyl-2,4,6,8-nonatetraen-1-al.

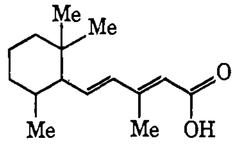
(2) C. L. Stevens and A. J. Weinheimer, *J. Am. Chem. Soc.*, **80**, 4072 (1958).

(3) H. Normant and M. deBotton, *Compt. Rend.*, **256**, 1996 (1963).

II was condensed with methyl β,β-dimethylacrylate (III) in the presence of potassium amide in liquid ammonia over a period of 48 hr. The product was decomposed with methanol–water and the work-up yielded acid IV: mp 110–111°; uv $\lambda_{\max}^{\text{MeOH}}$ 261 mμ (ϵ 21,000); ir (KBr): broad absorption at 3200–2600 (carboxyl), 1675 ($\nu_{C=O}$), 1620, 1590 ($\nu_{C=C}$), 1445 ($\delta_{as\text{-}CH_3}$), 1375 ($\delta_{s\text{-}gem\text{-}CH_3}$), 1255 ($\nu_{C-OH}$), and 975 cm^{-1} ($\delta_{CH}$ of *trans* double bond); mass spectrum, molecular ion at *m/e* 236 (calculated for $C_{15}H_{24}O_2$, 236). The configuration about the newly formed double bond is *trans* from spectral data and is also in accord with earlier findings[4,5] on similar condensations.[6] Acid IV was smoothly reduced to alcohol V by means of lithium aluminum hydride in anhydrous ether solution in quantitative yield. V was obtained as an oil and purified by distillation: bp 108° (0.08 mm); uv $\lambda_{\max}^{\text{MeOH}}$ 237 mμ (ϵ 25,200); ir (neat): 3340 (ν_{OH}), 1630, 1595 ($\nu_{C=C}$), 1447 ($\delta_{as\text{-}CH_3}$), 1375 ($\delta_{s\text{-}gem\text{-}CH_3}$), 1010 ($\nu_{C-OH}$), and 960 cm^{-1} ($\delta_{CH}$ of *trans* double bond); mass spectrum, P − 1 peak at 221 (calculated for $C_{15}H_{26}O$, 222); nmr: 1 H, doublet at τ 3.75 (J = 16 cps), 2 H, complex multiplet at 5.42, 2 H, doublet at 5.80 (J = 7 cps), 1 H, broad singlet at 6.74, 3 H, sharp singlet at 8.20, 6 H, singlet at 9.21, and a complex region, 7.80–9.30. V was oxidized with "active" manganese dioxide[7] in carbon tetrachloride solution to give the aldehyde VI, purified in 62% yield by distillation: bp 96–98° (0.07 mm); uv $\lambda_{\max}^{\text{EtOH}}$ 285 mμ (ϵ 28,900); ir (neat): 2740 (ν_{CHO}), 1665 ($\nu_{C=O}$), 1627, 1580 ($\nu_{C=C}$), 1448 ($\delta_{as\text{-}CH_3}$), 1357 ($\delta_{s\text{-}gem\text{-}CH_3}$), and 960 cm^{-1} ($\delta_{CH}$ of *trans* double bond); mass spectrum, molecular ion at *m/e* 220 (calculated for $C_{15}H_{24}O$, 220). The 2,4-dinitrophenylhydrazone derivative of VI was prepared as red crystals: mp 182–185°; uv $\lambda_{\max}^{\text{MeOH}}$ 392 mμ. Attempted purification of the aldehyde by column chromatography on neutral alumina was frustrating since the compound extensively decomposed on the column.



II



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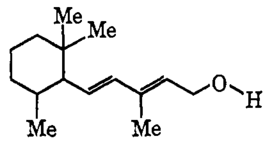
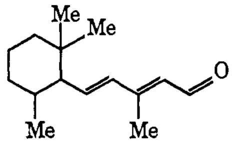
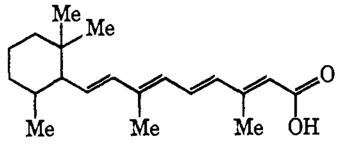


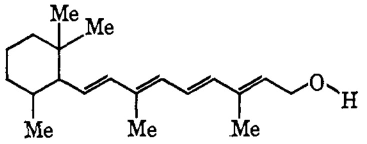
V



VI



VII



VIII

Repetition of the base-catalyzed condensation of III with VI in the presence of potassium amide furnished acid VII[8] in 63% yield: mp 157–158°, pale yellow needles from ethanol; uv $\lambda_{\max}^{\text{MeOH}}$ 325 mμ (ϵ 40,000); ir (KBr): broad absorption at 3200–2700 (carboxyl), 1678 ($\nu_{C=O}$), 1588 ($\nu_{C=C}$), 1450 ($\delta_{as\text{-}CH_3}$), 1375 ($\delta_{s\text{-}gem\text{-}CH_3}$), 1250 ($\nu_{C-OH}$), and 965 cm^{-1} ($\delta_{CH}$ of *trans* double bond); mass spectrum, no molecular ion was observed but a P − 44 peak (at *m/e* 258) was prominent, presumably caused by loss of carbon dioxide (calculated for $C_{20}H_{30}O_2$, 302). Reduction of VII with $LiAlH_4$ in ether yielded alcohol VIII as a viscous yellow oil in near-quantitative yield. It was analyzed by thin layer chromatography on silica gel G and found to be homogeneous. It was further characterized by the following: uv $\lambda_{\max}^{\text{MeOH}}$ 323.0 (ϵ 28,100), 308.0 (35,300), and 295.0 mμ (26,800); ir (neat): 3320 (ν_{OH}), 1610 ($\nu_{C=C}$), 1450 ($\delta_{as\text{-}CH_3}$), 1380 ($\delta_{s\text{-}gem\text{-}CH_3}$), 1000 ($\nu_{C-OH}$), and 960 cm^{-1} ($\delta_{CH}$ of *trans* double bond); mass spectrum, molecular ion at *m/e* 288 (calculated for $C_{20}H_{32}O$, 288).

We have oxidized the above alcohol to *all-trans*-5,6-dihydroretinal (IX), with "active" manganese dioxide.[7] However, *all-trans*-IX will not interact with opsin. Preliminary experiments[9] indicate that an irradiated (at 425 mμ) sample of IX couples with cattle opsin to form a synthetic visual pigment which exhibits $\lambda_{\max}$ 463 mμ. We believe that during the process of irradiation either the 9-*cis* or the 11-*cis* or both of these isomers of IX are formed. Just as in the case of visual pigments formed from retinal and 3-dehydroretinal, the visual pigment formed from irradiated IX also undergoes bleaching when exposed to white light. Further characterization of the pigment is in progress and will be reported separately.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. NB 06712-02.

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[4] M. Matsui, K. Yamashita, M. Miyano, S. Kitamura, S. Okano, A. Kobayashi, T. Sato, and R. Mikami, *J. Vitaminology* (Tokyo), **4**, 190 (1958).

[5] U. Schwieter, C. von Planta, R. Ruëgg, and O. Isler, *Helv. Chim. Acta*, **45**, 528 (1962).

[6] A detailed study of the nmr spectra of IV and several other related compounds are in progress and will be reported later.

[7] Supplied by General Metallic Oxides Co., Jersey City, N. J.

[8] All new compounds (IV, V, VI, VII, and 2,4-dinitrophenylhydrazone of VI) gave satisfactory elemental analyses.

[9] Performed by Dr. Peter B. Dewhurst in our laboratories.

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A Thiocarbonyl Complex of Iron

Sir:

The thiocarbonyl complexes, *trans*-$RhX(CS)[P(C_6H_5)_3]_2$, where X = Cl or Br, have been recently prepared[1] by the reaction of $RhX[P(C_6H_5)_3]_3$ with CS_2 in the presence of excess $P(C_6H_5)_3$ and CH_3OH. These complexes were also oxidized with halogen, X_2, to the octahedral $RhX_3(CS)[P(C_6H_5)_3]_2$. In this communication we report the synthesis of $[C_5H_5Fe(CO)_2(CS)]PF_6$

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[1] M. C. Baird, G. Hartwell, Jr., and G. Wilkinson, *J. Chem. Soc., A*, 2037 (1967).