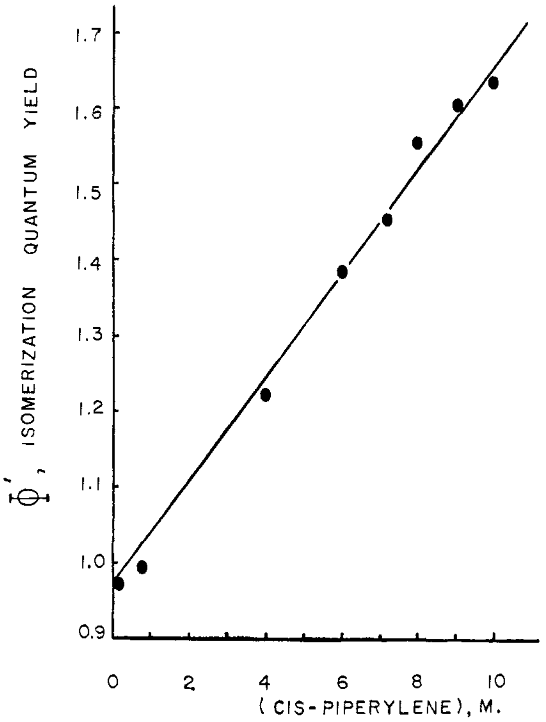

Figure 1. Benzophenone-sensitized *cis–trans* isomerization quantum yields as a function of *cis*-piperylene concentration: concentration of benzophenone, $2 \times 10^{-2}$ *M;* 366-nm excitation.

In view of the isomerization yields exceeding unity in the case of benzophenone, the interaction of the piperylene triplet with its ground state is an inviting possibility. The following two reactions could lead to isomerization efficiencies greater than unity

$$P^{*3} + cis\text{-}P \longrightarrow trans\text{-}P + P^{*3} \qquad (2)$$

$$P^{*3} + cis\text{-}P \longrightarrow \begin{bmatrix}\text{diradical addition}\\ \text{to ground state}\end{bmatrix} \rightsquigarrow \alpha\, cis\text{-}P + (2 - \alpha)trans\text{-}P \quad (\alpha < 1) \qquad (3)$$

where $P^{*3}$ is the piperylene triplet that decays to either *cis* or *trans* isomer. The overall effect in reaction 2 is to isomerize a *cis* molecule, while still maintaining a triplet piperylene for isomerization. In reaction 3, diradical addition to the ground state followed by fragmentation may lead to a predominance of *trans* molecules in their ground state. Both reactions result in isomerization enhancement involving a triplet state and a ground state molecule of piperylene. The triplet state energies for the *cis* and *trans* isomers have been reported to be: *cis*-piperylene = 57 kcal, *trans*-piperylene = 59 kcal.[1,4] Although piperylene has been shown to quench singlet states of aromatic hydrocarbons,[5] the singlet lifetime of benzophenone ($\leq 10^{-10}$ sec) is probably too short-lived to be quenched; consequently, it would appear that only the benzophenone triplet is involved in the sensitization process. Inclusion of reactions 2 and 3 into the present reaction scheme results in eq 4, where $k_x$ is the combined rate

$$\Phi' = \phi_T[1 + k_x(cis\text{-}P)/k_{dt}'] \qquad (4)$$

constant for reaction between the piperylene triplet and *cis*-piperylene in the ground state, and $k_{dt}'$ is the rate constant for deactivation of the piperylene triplet to a *trans*-ground state. This equation predicts a linear relationship between $\Phi'$ and (*cis*-P), with an intercept equal to $\phi_T$, which is unity for benzophenone. The results of the experiments in this laboratory are plotted in Figure 1 and obey eq 4 satisfactorily. It can be seen that the intercept is indeed unity within experimental error. Determination of the slope from Figure 1 indicates a ratio of 0.064 $M^{-1}$ for $k_x/k_{dt}'$. It should be noted that the actual sensitized *cis–trans* isomerization yield of *cis*-piperylene has increased from 0.55 to 0.90 in the concentration range studied. Since the lifetime of the piperylene triplet is unknown, it is difficult to determine an accurate value for $k_x$; however, Hammond, *et al.*,[6] have estimated that diene triplets live at least $5 \times 10^{-6}$ sec and probably longer. Using their value for $k_{dt}'$, the value of $k_x$ is estimated to be $\sim 1.3 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. The low value for $k_x$ is surprisingly close to the value for diradical addition of the isoprene to its ground state to form dimers,[6] and suggests that possibly reaction 3 may be the source for isomerization enhancement.

There is the need for caution in determining the triplet yield of a sensitizer by *cis–trans* isomerization, since disappearance of *cis*-piperylene *via* dimerization could lead to high values of $\Phi_{c\rightarrow t}$ when analysis is determined by vpc of the *cis–trans* ratios.[7] The data of this paper were obtained by the following two methods: (a) *cis–trans* isomerization ratios and (b) direct comparison of *trans* concentration with known solutions. Although method a gave consistently higher results than method b, the agreement was within 10%. It follows, therefore, that dimerization is not a major contribution to the triplet counting experiments.

The above effect does not alter triplet yield determinations reported in the literature, since their determinations are performed at piperylene concentration <1.0 *M*. It is not unexpected, however, that other olefins may show similar enhancement at high concentrations.

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## Stabilization of a Thioketocarbene through π-Complex Formation. Synthesis and Structure of *Trihapto*-1,2-diphenylthioketocarbene–Hexacarbonyldiiron

*Sir:*

Thioketocarbenes are hypothetical 1,3 dipoles,[1] which have been implicated as intermediates in the thermolysis of 1,2,3-benzothiadiazole[2] or the photolysis of 4-phenyl-1,2,3-thiadiazole.[3] 1,2-Diphenylthioketocarbene, $(\ddot{C}_6H_5)C({=}S)CC_6H_5$ (**2**), has been suggested to occur in the pyrolysis of certain metal dithienes,[4]

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(1) See R. Huisgen, *Angew. Chem.*, **75**, 604, 741 (1963); *Angew. Chem. Int. Ed. Engl.*, **2**, 565, 633 (1963), for general discussion.

(2) R. Huisgen and V. Weberndörfer, *Experientia*, **17**, 566 (1961).

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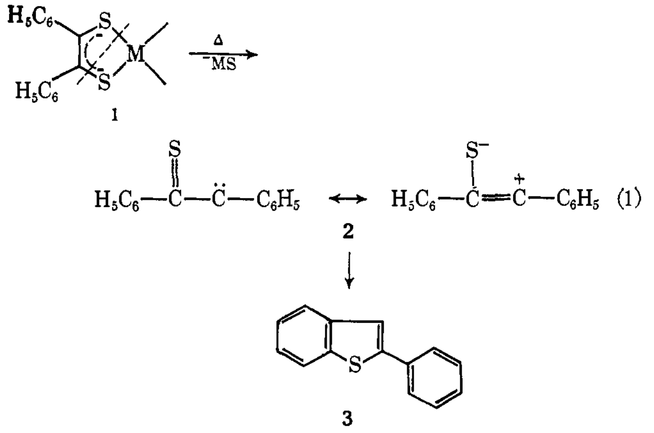
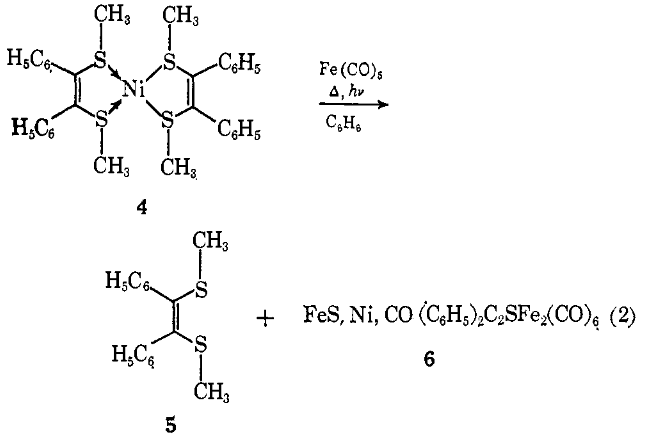


and could account for the demonstrated formation of 2-phenylthianaphthene (3) according to eq 1. While studying the degradation of dialkyl derivatives of nickel(II) bis-*cis*-ethylenedithiolates[5] with $Fe(CO)_5$, we have obtained a complex which appears to be the first example of a compound containing a coordinated thioketocarbene moiety. Refluxing-irradiating complex **4** in benzene solution in the presence of excess $Fe(CO)_5$ with a 150-W tungsten light source afforded *cis*-$\alpha,\alpha'$-bismethylthiostilbene (5)[5] and an orange, crystalline complex of composition $(C_6H_5)_2C_2SFe_2(CO)_6$ (6), mp 125–126° dec, after recrystallization from $CH_2Cl_2$-$CH_3OH$ (eq 2). The reaction is accompanied by the formation of a metal mirror consisting almost entirely of nickel. This suggests that a volatile nickel compound, probably $Ni(CO_4)$, is formed during the reaction and subsequently decomposes on the walls of the reaction vessel. *Anal.* Calcd for $C_{20}H_{10}O_6SFe_2$ (6): C, 49.04; H, 2.06; O, 19.60; S, 6.56; Fe, 22.80; mol wt, 489. Found: C, 49.24; H, 2.10; O, 19.50; S, 6.60; Fe, 22.35; mol wt, 495 (osmometrically in $CH_3CHCl_2$). On heating, **6** decomposes into FeS, Fe, CO, and diphenylacetylene. The infrared spectrum of **6** in KBr indicates metal carbonyl bands at 2066, 2033, 2010, and 1957 $cm^{-1}$, but none in the bridging or ketonic carbonyl range. Two separate signals of the phenyl protons in the $^1H$ nmr spectrum in $CDCl_3$ (sharp signal at 7.16, a group of signals centered around 7.10 ppm) reveal a structural asymmetry, thus eliminating a complex containing coordinated diphenylthiirene or symmetrically bonded diphenylacetylene and sulfur. On the basis of these results **6** was considered to be a $\pi$ complex of 1,2-diphenylthioketocarbene, a view which in turn was confirmed by an X-ray crystallographic structure determination.



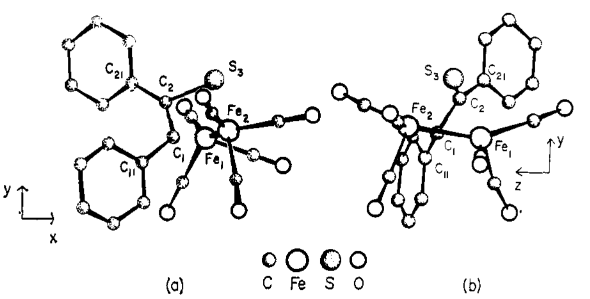


Figure 1. The structure of the $(C_6H_5)_2C_2SFe_2(CO)_6$ complex (6) viewed along (a) the *z* axis, and (b) the *x* axis.

Crystals of **6** belong to the monoclinic system with $a = 16.006\ (14)$, $b = 9.455\ (8)$, and $c = 13{,}159\ (7)$ Å, and $\beta = 101°\ 18'\ (3')$. There are four molecules of $C_{20}H_{10}O_6SFe_2$ (6) in the unit cell and the space group is $P2_1/c$. The structure was determined from 2984 reflexions collected on a Picker FACS-1 diffractometer with Mo K$\alpha$ radiation (Nb filter), and, at the present time, has been refined to an *R* factor of 0.052 on all nonzero data. Views of the nonhydrogen atoms are shown in Figure 1.

The thioketocarbene moiety is asymmetrically coordinated to the two iron atoms. The $Fe_1$–$Fe_2$ distance is 2.533 (1) Å, the $Fe_1$–$C_1$, $Fe_1$–$C_2$, and $Fe_1$–$S_3$ distances are 2.089 (6), 2.061 (6), and 2.243 (2) Å, respectively, while the $Fe_2$–$C_1$, $Fe_2$–$C_2$, and $Fe_2$–$S_3$ distances are 1.969 (7), 2.654 (6), and 2.256 (2) Å. The Fe–Fe length falls within the limits of the Fe–Fe distances compiled by Churchill,[6] while the two Fe–S distances are in good agreement with those usually found in molecules where sulfur is coordinated to iron carbonyl groups.[7–9] The $C_1$–$C_2$ and $C_2$–$S_3$ lengths are 1.393 (9) and 1.756 (6) Å, while the $C_{21}$–$C_2$–$S_3$, $C_{21}$–$C_2$–$C_1$, $C_1$–$C_2$–$S_3$, and $C_2$–$C_1$–$C_{11}$ angles are 121.6 (4), 135.0 (6), 103.3 (5), and 124.3 (5)°, respectively. The very small $C_1$–$C_2$–$S_3$ angle may indicate internal strain or some interaction between $C_1$ and $S_3$ (distance 2.481 (6) Å). The $C_1$–$C_2$ bond is significantly longer than the (S)C═C(S) bonds in the two crystallographically independent molecules of $\mu,\mu'$-(*cis*-stilbene-$\alpha,\beta$-dithiolato)-bis(tricarbonyliron).[7] The atoms $C_{11}$ and $C_{21}$ are displaced in the same direction by 0.295 and 0.080 Å from the plane defined by $C_1$, $C_2$, and $S_3$.

The shortness of the $Fe_2$–$C_1$ distance suggests that this bond is essentially $\sigma$ in character. The near identity of the distances between $Fe_1$, $C_1$, and $C_2$, respectively, as well as the spatial arrangement of $Fe_1$ relative to $C_1$ and $C_2$ indicate a predominance of $\pi$ bonding interactions between $Fe_1$ and the 1,3 dipole ligand, leading to a delocalized bonding situation schematically represented by formula **7**. The remarkable bonding bifunctionality of the ligand in **6** is completely consistent with its intermediate thioketocarbene 1,3-dipolar structure as symbolized by formulas **2**. The successful stabilization of a

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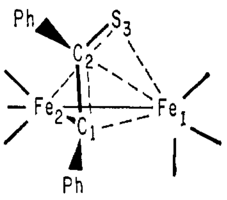

**7**

thioketocarbene through π-complex formation is of interest concerning the nature and mechanism of 1,3-dipolar cycloaddition reactions and can probably be extended to other reactive intermediates of this general type.

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## Conformational Analysis of a Minor Nucleoside from Nuclear Magnetic Resonance Data. Pseudouridine

*Sir:*

We report here a complete analysis of the 100-MHz nmr spectrum of β-pseudouridine (βψ), and the resulting model for the three-dimensional structure. A 60-MHz spectrum has previously appeared,[1] but no detailed analysis was attempted. βψ is a modified nucleoside found in all tRNA sequenced to date.[2,3] It differs from the normal nucleosides in that the uracil is attached to the ribose *via* a C–C glycosyl bond, making the NH group at position one available for hydrogen bonding (Figure 1).

The 100-MHz spectrum was analyzed using the computer program LAOCOON II[4] modified to give spin-tickling information. A simulated spectrum for the 2′–5′ hydrogens is shown above the relevant portion of Figure 1. The assignment was confirmed by double irradiation. The resultant shifts and coupling constants are in Table I. βψ was a product of Calbiochem. Anomeric purity was confirmed by comparison of the nmr data with those for the α anomer.

The data allow three important conclusions to be made regarding (i) rotamer population about the exocyclic $C_{4'}$–$C_{5'}$ bond, (ii) puckering of the ribose ring, and (iii) the sugar–base torsion angle.

(i) The vicinal proton coupling constants are known to depend on the relevant dihedral angles.[5] Thus, $J_{4',5'B}$ and $J_{4',5'C}$ yield information about the relative rotamer populations. The following assumptions are made in the analysis: the *J*'s are rapid time averages weighted over the classical staggered rotamers; the *gauche* and *trans* couplings do not vary among the rotamers; the Karplus equation as modified by Abraham, *et al.*,[6] for carbohydrates applies. Therefore $J_{4',5'B} = 2(P_I + P_{II}) + 10.1P_{III}$, and $J_{4',5'C} = 2(P_I + P_{III}) + 10.1P_{II}$ Hz, where the $P_i$ are fractional populations $\left(\sum_{i=I}^{III} P_i = 1\right)$. The calculated $P_i$ are given in Figure 2. The preferred conformation in aqueous solution is apparently the *gauche–gauche* rotamer in which the 5′-OH lies above the ribose. Although X-ray data are lacking for βψ, those obtained for a wide variety of nucleosides, nucleotides, and polyadenylic acid indicate that this rotamer occurs most frequently in the solid state.[7,8] To the best of our knowledge this is the first experimental evidence for a preferred conformation about the exocyclic $C_{4'}$–$C_{5'}$ bond of a nucleoside in solution.

**Table I.** Proton Chemical Shifts and Coupling Constants of β-Pseudouridine and Uridine[a]

| | Chemical shifts (ppm)[b] | | | | Coupling constants, Hz[b] | | |
|---|---|---|---|---|---|---|---|
| | βψ | | U | | βψ | | U |
| | 30° | 70° | 28° | | 30° | 70° | 28° |
| $H_6$ | 7.660 | 7.627 | 7.850[c] | $J_{6,1'}$ | 0.8 | 0.8 | <0.5 |
| $H_{1'}$ | 4.674 | 4.668 | 5.820 | $J_{1',2'}$ | 5.0 | 5.2 | 4.4 |
| $H_{2'}$ | 4.279 | 4.260 | 4.260 | $J_{2',3'}$ | 5.0 | 5.0 | 4.6 |
| $H_{3'}$ | 4.141 | 4.128 | 4.150 | $J_{3',4'}$ | 5.2 | 5.2 | 4.9 |
| $H_{4'}$ | 4.009 | 3.993 | 4.060 | $J_{4',5'B}$ | 3.2 | 3.4 | |
| $H_{5'B}$ | 3.840 | 3.825 | 3.825 | $J_{4',5'C}$ | 4.6 | 4.8 | |
| $H_{5'C}$ | 3.726 | 3.719 | 3.735 | $J_{5'B,5'C}$ | −12.7 | −12.4 | |

[a] S. Fujiwara and M. Uetsuki in "Recent Developments of Magnetic Resonance in Biological Systems," S. Fujiwara and L. H. Piette, Ed., Hirokawa Publishing Company, Inc., Tokyo, 1968, p 1. [b] The chemical shifts and coupling constants are estimated to be accurate to within 0.003 and 0.1 Hz, respectively. [c] B. J. Blackburn, unpublished results.

(ii) If the ribose ring of βψ existed in any of the conventional puckered or planar conformations, large differences in $J_{1',2'}$, $J_{2',3'}$, and $J_{3',4'}$ would exist, as compiled in Table II. These large differences enable one to use the Karplus equation, despite its known qualifications,[9] to determine the conformation of the ribose ring. Examination of Table II shows that a single conformation predicts neither the near equality of $J_{1',2'}$, $J_{2',3'}$, and $J_{3',4'}$, nor their observed magnitudes. This suggests that either a rapid interconversion exists between the $C_{2'}$-*endo* and $C_{3'}$-*endo* (or $C_{2'}$-*exo* and $C_{3'}$-*exo*) forms, or that the 2′, 3′, 4′ section of the ribose ring is planar. If the latter were true, however, $J_{2',3'}$ should be equal to approximately 9 Hz. Thus, an interconversion must take place, in which the hydroxyl groups at $C_{2'}$ and $C_{3'}$ pass through the eclipsed conformation. The data also exclude the possibility of a simple equilibrium between the 2′-*endo* and 3′-*exo* conformations (since $J_{1',2'} = J_{3',4'}$). The apparent lack of rigidity in the ribose ring in solution must be taken into account in theoretical calculations of polynucleotide

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