BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3323—3328 (1971)

Theoretical and Experimental Considerations of the Direct Photo-Isomerization and Chemistry of 1,3-Pentadiene

Kozo Inuzuka* and Ralph S. Becker
Department of Chemistry, University of Houston, Houston, Texas 77004, U. S. A.

(Received June 24, 1971)

Potential energy curves as a function of the angle of twist around single and double bonds have been calculated for piperylene (1,3-pentadiene). Also, direct-excitation *cis*→*trans* photoisomerization and *trans*→methylcyclobutene photochemistry have been investigated as a function of the temperature. The theoretical analysis strongly indicates that the cyclobutene is formed photochemically from the *trans-s-cis* isomer which is created thermally from the *trans*-isomer in the ground state (not by photoisomerization). The temperature-dependency data support this conclusion. The theoretical data also indicate that there is a small barrier to photoisomerization around the double bond in the first excited singlet (and triplet) state. The temperature-dependency data also support this conclusion. The potential energy curves are in harmony with the known emission (none exists), photoisomerization, and internal-conversion data for the *cis*- and *trans*-piperylenes. The emission properties of model cyclic diene steroids are compared with those expected from linear dienes, and the emission results of the former are interpreted within the theoretical framework developed.

The direct photoirradiation of a cyclohexane solution of piperylene at 2537 Å results in the formation of 3-methylcyclobutene and *cis-trans* isomerization as the main reactions.[1] On the other hand, the sensitized photoisomerization of piperylene has also been studied in detail using a variety of sensitizers.[2–5] The experimental data show that there is a photostationary equilibrium between *cis*- and *trans*-piperylene, and also that other photoproducts are produced.[3] The concentration ratio of *cis*- and *trans*-isomers depends on the lowest triplet energy of the sensitizer.[2,5] The theoretical consideration of the photochemical mechanisms appropriate to piperylene are more difficult than in the case of butadiene. The introduction of the methyl group in the terminal carbon atom brings about a steric effect in piperylene, and also the methyl group may have some inductive and resonance effects on the π-electron system of the molecule. In this investigation we made the general assumption that the substitution of a methyl group into the terminal methylene of butadiene does not produce any significant effect on the π-electron structure of butadiene. Therefore, calculated results of the potential energy curves of butadiene can be used to explain the mechanism of the *cis-trans* isomerization of piperylene. However, we have specifically included the non-bonded interaction effect between the methyl group and the other atoms of piperylene at the *cis*-side, at the *trans*-side, and for the form twisted by 90 around the double bond (*vide infra*).

Methods of Calculation

The following numerical values[6] were used for the skeletal structure of *trans*-1,3-butadiene: 1.339 Å for the carbon double bond and 1.480 Å for the central single bond. The value of 123° was assigned to the bond angle, ∠CCC. The skeletal structure only was taken into account. All the calculations were carried out within the framework of the general semiempirical SCF–MO–CI method, and the Pariser-Parr approximation was used for the electron repulsion integrals. The resonance integral for the nearest neighbor carbon atom, β_{CC} was treated as a parameter and adjusted to fit the calculated lowest π,π^* state

---

* Present address of K. I., Department of Applied Science, Tokyo, Electrical Engineering College, Kanda, Chiyoda-ku, Tokyo, Japan. U. S. A. reprint requests should be directed to R. S. B.

[1] a) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962). b) S. Boue and R. Srinivasan, *ibid.*, **92**, 3226 (1970).

[2] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

[3] G. S. Hammond, N. J. Turro, and R. S. H. Liu, *ibid.*, **28**, 3297 (1963).

[4] G. S. Hammond, N. J. Turro, and P. A. Leermakers, *ibid.*, **83**, 2396 (1962).

[5] N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969).

[6] B. P. Stoicheff, "Advances in Spectroscopy," **1**, (1959), Wiley-Interscience, New York, p. 148.

[7] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

energy to the experimental value. The β_{CC} for the twisted bond was obtained from the following equation:

$$\beta(\theta)=\beta_{CC}\cos\theta \qquad (1)$$

where θ is the angle of twist. All the penetration terms were neglected. In the present paper, calculations concerning the single-bond twist and the terminal double-bond twist were carried out.

In the case of double-bond twisting, the effect of the bond twist upon the electron repulsion integrals was taken into account (*vide infra*). In the case of single-bond twisting, the foregoing concern was neglected because such neglect did not have any significant effect upon the final result. We calculated the state energies of the molecule as it is twisted about the single or double bond using the SCF–MO's obtained. All singly-excited configuration interactions were taken into account (complete single excited-state configurational interaction). Furthermore, in the case of the double-bond twist, all doubly-excited configuration interactions were also taken into account (complete single and double excited-state configurational interaction). The total π-electron energy, E, in the ground state is obtained by:

$$E = E_\pi + E_n \qquad (2)$$

where E_π is the energy of the π electrons and where E_n is an effective nuclear interaction term given by Pople:[8]

$$E_n = \sum_{\mu<\nu} Z_\mu Z_\nu / R_{\mu\nu} \qquad (3)$$

Z_μ is the effective charge of the atom, μ; unity is used for Z_μ in the present calculation. The potential energy curves for the ground state are obtained by the calculation of the total π electron energy, E, as a function of the angle of twist. The potential energy curves of the excited states, as a function of the angle of twist, are obtained by superimposing the state energies upon the potential curve of the ground state.

Before the calculation of the twisting around the double bond of 1,3-butadiene was carried out, the general SCF–MO–CI method was used to calculate the shape of the potential energy curves for twisted ethylene in order to verify its utility. The calculated potential energy curve of the triplet state[9,10] is in harmony with the experimental results on the photoisomerization of *cis* and *trans*-1,2-dichloroethylene. To produce such potential minima in the excited states of ethylene at 90° (within the framework of the semiempirical SCF–MO–CI with zero differential overlap using the point charge atomic repulsion integral), the following function was used for the atomic repulsion integral of the atoms of the terminal double bond:[12]

$$\gamma_{C=C}(\theta) = \gamma_{C=C}(0) + A(1-\cos\theta) \qquad (4)$$

where the first term corresponds to the planar atomic repulsion integral value, where θ is the angle of twist, and where A is a parameter. All the other atomic repulsion integrals were calculated by the Pariser-Parr equation without any correction. In addition, the twisting around any bond will result in the introduction of $2p\sigma$ components into the atomic repulsion integrals between the *non-nearest* neighbor atoms.[12] This effect will make an atomic repulsion integral value larger than the one with only a pure $2p\pi$ component corresponding to the same bond distance. To take this effect into account, an off-center position was assumed for the location of the center of the atoms involved. As the simplest method, the off-center positions were taken on the same side of the $2p\pi$ orbitals and by some small distance off the center of the atom along the $2p\pi$ atomic-orbital axis. This off-center distance was looked upon as the parameter. The calculation was carried out over the angles from 0° (planar form) to 85° (the nearperpendicular form).

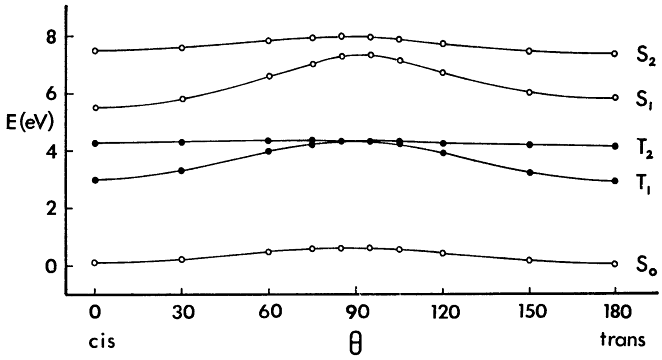


Fig. 1. Potential energy curves for ground and excited states of 1,3-butadiene as a function of angle of twist around the single bond using Eq. (1) ($\beta_{C=C}=-2.70$ eV and $\beta_{C-C}=-2.00$ eV) and including all singly excited configurations.

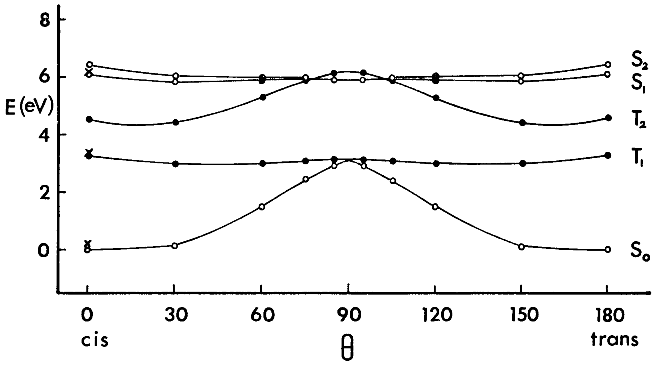


Fig. 2. Potential energy curves for ground and excited states of 1,3-butadiene as a function of angle of twist around a double bond using Eqs. (1) ($\beta_{C-C}=-2.00$ eV and $\beta_{C=C}=-2.70$ eV), (4) ($\gamma_{C=C}=7.503$ eV and $A=0.5$ eV), an off-center value of 1.0A and including all singly and doubly excited configurations. The X points are the energy values including non-bonding interaction (see text).

---

8) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

9) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 526 (1948).

10) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

11) Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1969).

12) R. S. Becker, K. Inuzuka, and J. King, *J. Chem. Phys.*, **52**, 5164 (1970); R. S. Becker, K. Inuzuka, J. King, and D. E. Balke, *J. Amer. Chem. Soc.*, **93**, 43 (1971).

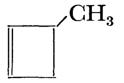
The results calculated using these approaches are shown in Figs. 1 and 2.

Results and Discussion

The potential energy curves of 1,3-butadiene twisted around the central bond are shown in Fig. 1.

The potential energy curves resulting from twisting around the double bond are shown in Fig. 2, where these potential energy curves are shown to be symmetric with respect to the twisting angle, 90° since all effects of the hydrogen atoms are neglected. These potential energy curves show that the energies of the T_1, S_1, and S_2 states decrease with an increase in the twisting angle around the double bond. The potential curve for T_1 is almost degenerate with the ground state at 90°. The potential energy curve, T_2, has a maximum at 90°, and it crosses the two potential curves S_1 and S_2 near 80°. The introduction of a methyl group in the position of the terminal hydrogen atom of butadiene will make the potential energy curves of butadiene asymmetric with respect to 90°. The spectroscopic data for the S_1 and T_1 of *cis*- and *trans*-piperylene were used to make a rough estimation of the shape of the potential energy curves of piperylene on the *cis*- and *trans*-sides. The absorption spectra of *cis*- and *trans*-piperylene[13] in an *n*-heptane solution have the $S_0 \rightarrow S_1$ band maxima at 225 nm for the *cis*-form and at 222 nm for the *trans*-form. The difference between the band maximum of the isomers is about 0.1 eV. From the S–T absorption data,[14] the $S_0 \rightarrow T_1$ transition energy of the *trans*-form may be seen to be higher than that of the *cis*-form by about 0.1 eV. The non-bonding interaction energies between the methyl hydrogen atoms and the other atoms of the residual part at the twisting angle, 0, 90, and 180°, using 180° (*trans*) as a reference, were calculated by using Bartell's equations.[15] These values reached their maxima at the *cis*-side (0°) and their minima at 90°. These calculated results show that the non-bonding interaction energy between the methyl group and the residual part of the molecule is negligible for the *trans* (180°) and perpendicular (90°) forms. The non-bonding energy value gave, at most, an energy increase of 0.2 eV for the *cis*-form. As these calculated values correspond to the maximum interaction energy value for each form, the actual non-bonding interaction energy value may be smaller than the value calculated. This calculated value, 0.2 eV, can be superimposed on the calculated ground-state and excited-state potential energy curves of butadiene at 0° (*cis*-form). A consideration of the spectroscopic differences for the $S_0 \rightarrow S_1$ (0.1 eV) and $S_0 \rightarrow T_1$ (0.1 eV) transitions and the non-bonding interaction energy suggests that the lowest excited singlet and triplet states of piperlylene are higher by ≤ 0.1 eV on the *cis*-side than on the *trans*-side (Fig. 2). Therefore, the potential energy curves will be asymmetric around 90° and isomerization should be easier from the *cis*-side than from the *trans*-side (*vide infra*).

The direct irradiation of a mixture of *cis*- and *trans*-piperylene[1)] initially gives rise to an increase in the *cis*-piperylene, while the *trans*-piperylene decreases. The 3-methylcyclobutene originates primarily from the *trans* isomer[1)] as:

trans-piperylene $\xrightarrow{h\nu}$  (5)

The following reaction[1)] also occurs concurrently:

$$\textit{trans}\text{-piperylene} \xrightarrow{h\nu} \textit{cis}\text{-piperylene} \tag{6}$$

The irradiation of 1,3-butadiene is known to give rise to cyclobutene.[1,16)] This process apparently occurs from the excited singlet state of 1,3-butadiene.[16)] This suggestion may also be applicable to the process of the cyclization of piperylene, because the structure of piperylene is parallel to that of 1,3-butadiene. Figure 2 shows that, in the ground-state, twisting around the terminal double bond has a very high potential barrier near 90°. This suggests that the twisting around the terminal double bond of butadiene is very difficult because of the high activation energy. However, the potential curves for the lowest excited singlet and triplet states show that there is a shallow minimum at 30–50° and a small barrier (~0.03 eV) beyond 60° in S_1, and that there is a shallow minimum at 35–60° and a low barrier (~0.1 eV) near 90° in T_1 (Fig. 2). The numerical values for the potential minimum and the barrier height in S_0, S_1, and T_1, and the other states depend on the choice of the parameters; that is, the off-center values, A in Eq. (4) and the approximation used for the electron repulsion integral, *etc.* However, within our present procedure, changes in the magnitude of the parameters for the off-center value and the A value in Eq. (4) result in potential energy curves similar in shape to those in Fig. 2. Those results suggest that a twisted form around the terminal double bond is more stable than the planar forms in S_1 and T_1. Also, Fig. 2 shows that the potential energy curve of T_1 is almost degenerate with that of the ground state, at 90°.[17)] This situation in butadiene is very similar to that of piperylene with a slight modification resulting from a slight asymmetry around 90° (*vide supra*). Srinivasan[1)] proposed that 3-methylcyclobutene (III) comes primarily from *trans*-piperylene (I). The production of 3-methylcyclobutene from *trans*-piperylene could arise as follows:

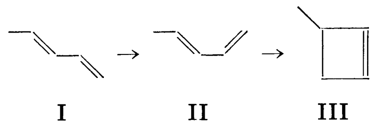
[13)] L. E. Jacobs and J. R. Platt, *J. Chem. Phys.*, **16**, 1137 (1948).

[14)] R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).

[15)] L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

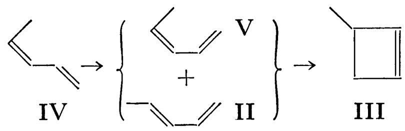
[16)] R. Srinivasan, *J. Amer. Chem. Soc.*, **85**, 4045 (1963).

[17)] The calculation was carried out through 0 to 85°. The potential energy curves of both states, S_0 and T_1 are not perfectly degenerated at 85°. Recently Eleveth [*Chem. Phys. Lett.*, **3**, 122 (1969)] carried out the calculation of the state energies of *trans*-butadiene at two twisted angles, 0 and 90°, using the different approach. His result shows that the both states, S_0 and T_1 are nearly degenerate at 90° but they are not perfectly degenerate.



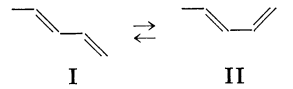
(7)

The very small production of 3-methylcyclobutene (III) originating from *cis*-piperylene (IV) could occur by the following process:



(8)

We will now examine the nature of the steps in the reaction (7). Figure 1 suggests that *s-cis*$\leftrightarrow$*s-trans* isomerization around a single bond of butadiene in the lowest excited states, S_1 and T_1 is difficult. Although there is a potential barrier for *s-cis*$\leftrightarrow$*s-trans* isomerization in the ground state, its height is quite low relative to those in S_1 and T_1. Figure 1 will be, in principle, also correct for the *s-cis*$\leftrightarrow$*s-trans* isomerization of piperylene around its single bond. These results thus clearly suggest that (1) the *trans-s-cis* piperylene (II) is not produced from *trans*-piperylene in an excited state, but in the ground state and, (2) that 3-methylcyclobutene is produced from II (*versus* I) photochemically. Furthermore, other recent theoretical research[18] suggests that the concentration of *s-cis*-butadiene in *s-trans* is about 3.2% at room temperature and that its concentration decreases on a decrease in the temperature. Therefore, *trans-s-trans*-piperylene in the ground state will be considered to be in thermodynamic equilibrium with the *trans-s-cis*-piperylene (II).



(9)

If *cis*-piperylene were to be the reactant, then reaction (8) would be the appropriate one to consider. The *trans-s-cis*-piperylene (II) is not expected to be produced from IV in the ground state because of the high energy requirement for double-bond isomerization. The *cis-s-cis*-piperylene (V) is not expected to be formed from IV in an excited state for reasons parallel to those given above concerning single-bond isomerization. Furthermore, because of the methyl-hydrogen steric interaction, the equilibrium concentration of the *cis-s-cis*-piperylene (V) produced from IV in the ground state is expected to be very small. Therefore, V will be of very little consequence in the production of the cyclobutene compound. It is potentially possible that (II) could be produced in the excited state of *cis*-piperylene, although the barrier to single-bond isomerization is present. This would involve excited-state double-bond isomerization, followed by a particular coupling, if internal conversion occurred (hot ground state *s-cis*$\leftrightarrow$*s-trans*); however, this reaction is not expected to occur with any appreciable efficiency. Thus, the formation of 3-methylcyclobutene from *cis*-piperylene is relatively unlikely, and the principal reactant is probably *trans*-piperylene *via* the intermediate (II). The relative importance of the *cis* and *trans* isomers in terms of the quantity of cyclobutene produced from them is in agreement with very recent quantitative findings[1b] published after this investigation was completed. The quantum yield of cyclobutene from the *trans* isomer is ~10 times that from the *cis* isomer.

Further verification exists for the source and mechanism proposed above for the production of the cyclobutene. According to our potential energy curves (Fig. 1), a *s-cis*$\leftrightarrow$*s-trans* equilibrium in the ground state would depend upon the temperature. That is, the concentration of *trans-s-cis*-piperylene (II) would decrease at low temperatures. Accordingly, the formation of the 3-methylcyclobutene photochemically produced should also *decrease at low temperatures.* The results of the direct irradiation of *cis-* and *trans*-piperylene[19] at different temperatures are shown in Table 1. In this experiment, the formation of 3-methylbutene is found from *trans*-piperylene, but essentially none is observed from *cis*-piperylene. The

TABLE 1. THE PHOTOCHEMISTRY OF PIPERYLENES AS A FUNCTION OF TEMPERATURE

Compound irradiated[a]	Temperature	Irradiation time	% conc.	3-methylcyclobutene
cis-piperylene	21°C	180 min	8.1 (trans)	essentially none observed
	−76°C	180 min	4.0 (trans)	essentially none observed
	21°C[d]	120 min	3.8 (trans)	essentially none observed
	−76°C[d]	120 min	2.1 (trans)	essentially none observed
trans-piperylene	21°C	100 min	—[b]	$4.6\times$[c]
	−76°C	100 min	—[b]	$1.5\times$[c]

a) In *trans*-1,2-dimethylcyclohexane by 200 W mercury arc lamp with Corning 9—54 filter (~220 nm cut-off, >70% transmission 254 nm).

b) It was not possible to determine the quantity of the *cis*-isomer produced. Quantities of *cis* and *trans* isomer determined by gas chromatography.

c) Numbers indicate quantity cyclobutene produced times that of a standard reference signal as determined by gas chromatography.

d) This represents a duplicate run under different experimental arrangements such that the absolute percent concentrations are different. However, note that ratio of the percent concentrations at the two temperatures is the same as that for the preceding set of data.

---

[18] L. M. Sverdlow and E. N. Bolotina, *Russ. J. Phys. Chem.*, **36**, 1502 (1962).

[19] J. Guillory, Phillips Pet. Co., Private Communication (1970).

experiment shows that the formation of 3-methylcyclobutene does *decrease with a decrease in the temperature*. Recently, van der Lugt and Oosterhoff[20)] performed theoretical calculations concerning the cyclization of *s-cis*-butadiene using a Valence Bond Procedure. Judging from their results,[20)] the photocyclization of *s-cis*-butadiene can occur relatively easily from the *s-cis* form in the excited singlet state. According to our experimental and theoretical data (those of others[18,20)]), the rate-determining step for the production of the cyclobutene from the *trans* isomer could well involve the formation of II from the *ground state* of *trans*-piperylene (Eqs. (7) and (9)). Also, it is possible that a barrier could exist in the excited state similar to that found for butadiene.[20)] An explanation for the difference in the amount of the cyclobutene from the *cis* and *trans* isomers was given earlier.

On the basis of the above discussion and reaction (9), it can be said that, when II is excited and the cyclobutene (III) is produced, the equilibrium between *trans-s-trans-* (I) and *trans-s-cis*-piperylene (II) should be reestablished. Thus, except for minor side reactions, eventually all of the *trans-s-trans*-piperylene (I) should be converted into (II) and the (II) into the cyclobutene (III). This is in agreement with the trend seen experimentally.[1)]

In the direct photoisomerization of the piperylene double bond, *cis-trans* isomerization is another important process. The *cis*↔*trans* isomerization of piperylene corresponds to the twisting around the terminal double bond (of butadiene). Figure 2 shows that the twisting of the double bond of butadiene can occur in the lowest singlet state. However, shallow potential energy minima exist at 30–50 and 150–120°, and small potential barriers are present at more highly twisted angles (*cf.* Fig. 2 and above). In the case of butadiene, the potential energy curves are symmetric with respect to 90° if the non-bonding interaction of all the H atoms is neglected. However, in the case of piperylene the effect of the methyl group should make the potential energy curve asymmetric with respect to 90° (*cf.* above and Fig. 2). Thus, we would predict *a temperature dependence for photoisomerization.* Our experimental results (Table 1) show that the *cis*-piperylene→*trans*-piperylene photoisomerization does occur *and that it is temperature-dependent.* Also, the photoisomerization of *trans*-piperylene→*cis*-piperylene can be expected, though it is 20% less than in the *cis*→*trans* process.[1b)] These facts suggest that the *cis*-piperylene→*trans*-piperylene isomerization is slightly dominant over the reverse reaction. Therefore, the potential energy curve of the lowest singlet state of piperylene could be slightly asymmetric with respect to 90°. Our potential energy curves do show an asymmetry that would be in agreement with the experimental results (*cf.* above and Fig. 2).

In addition to the formation of the cyclobutene (III), small quantities of 1,3-dimethylcyclopropene have been observed.[1b)] However, the quantity is very small compared with the amount of isomerization or even the amount of cyclobutene that results, particularly in the case of the *trans*-piperylene. It has been proposed that cyclopropylmethylene biradical intermediates are important in explaining the formation of the cyclopropene.[1b)] Also, it has been proposed that these same intermediates are important,[1b)] or are perhaps important,[21)] in the photoisomerization of 1,3-dienes. It is salient to point out that, in one case,[1b)] the difference in the photochemical reactivity of the *cis* and *trans* piperylenes was based on the fact that no barrier existed between the planar forms and the 90°-twisted forms in the excited singlet state. However, our experimental data (Table 1) strongly suggest that this is not true, at least for the *cis* isomer. Furthermore, our theoretical results indicate that a small barrier exists for twisting in the excited singlet state for both the *cis* and *trans* isomers (*vide supra*). In addition, some asymmetry appears to exist in the potential energy curves (*vide supra*). Finally, very recently serious doubt has been cast on the proposals that cyclopropylmethylene biradical intermediates are important in the photo *cis-trans* isomerization.[22)] This doubt has been based on the differences in the concentration dependences for the isomerizations and for the production of the cyclopropenes.[1b)]

There are four kinds of processes for the conversion of S_1 to S_0: fluorescence, internal conversion, intersystem crossing (with accompanying emission, internal conversion and photochemistry in triplet states), and photochemistry in S_1. No one has observed emission from a linear 1,3-diene at room temperature; this situation is very similar to that of acrolein, where the total quantum yield of emission is ~0.01[12)] (this point will be discussed more later). The total photochemical yields in solution are only about 0.10.[1b)] Further, there is a strong indication that ϕ_{IS} is less than 0.1.[21)] Thus, in piperylene, internal conversion directly from S_1 to S_0 must have a high quantum yield (~0.80). Figure 2 suggests that fluorescence is unlikely since torsional twisting has essentially no barrier and this latter process is expected to be fast (faster than fluorescence). The spin-orbit coupling is expected to be small in the carbon-hydrogen system except in special cases.[23)] Finally, Fig. 2 shows that, as the angle of twist increases, the energy separation between S_1 and S_0 decreases. Thus, the probability of internal conversion *via* vibronic coupling increases as the angle of twist increases from 0 toward 90°. Therefore, the foregoing considerations provide a good qualitative understanding of the experimental results obtained for piperylene. Pertinent to the discussion above, if internal conversion and photochemistry could be restricted, then fluorescence and/or phosphorescence should be observable. Although acrolein exhibits very little emission,[12)] model conjugated keto steroids show ϕ_p values of 0.2—0.3.[24)]

[20)] W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

[21)] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

[22)] J. Saltiel, private communication, 1971.

[23)] R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley-Interscience New York, N. Y. (1969).

[24)] G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chem. Acta*, **51**, 1890 (1968).

This has been interpreted in terms of the inability of such molecules to isomerize and to torsionally dissipate all of the energy; furthermore, spin-orbit coupling exists as well as vibronic coupling between the $T_{n,\pi}*$ and $T_{\pi,\pi}*$ states.[12] Furthermore, ergosterol and lumisterol$_2$ show fluorescence at 80°K.[25] Each of these molecules contain saturated ring systems fused to a cyclohexadiene ring. In these latter two cases, isomerization around a double bond in the excited singlet state should be prohibited and the rigidly bonded steroidal framework should prevent any noticeable torsional dissipation of energy. Thus, a potential energy minimum should exist at some small finite angle and fluorescence should occur. This is in agreement with the experimental results.[25] However, it should be noted that temperature and/or viscosity effects appear to be important since the foregoing steroids apparently do not emit at room temperature[25] even though the quantum yield of photochemistry is less than 1. Studies concerning these steroids and other polyenes are in progress.

Summary

Potential energy curves as a function of the angle of twist around single and double bonds have been calculated for 1,3-butadiene. In addition, these have been modified to apply to piperylene (1,3-pentadiene) by taking into account non-bonding interactions involving the methyl group. The results indicate that substantially higher barriers exist for twisting a single bond in the first excited singlet and triplet states than in the ground state. On the other hand, substantially lower barriers exist in the first excited singlet and triplet states for double-bond twisting compared to that in the ground state. On the basis of these and other considerations, we predicted that (1) cyclobutene should be photochemically produced from the *trans*-piperylene *via* the *trans-s-cis* isomer, (2) a temperature dependence should exist for cyclobutene production from the *trans* isomer because of a barrier to *s-cis-trans* isomerization in the ground state, and a possible barrier in the excited state and (3) very little cyclobutene should be produced from the *cis*-piperylene. All of these predictions are in harmony with the experimental results.

On the basis of the shape of the potential energy curves in the excited singlet (and triplet) states, we predicted that a barrier should exist for the inter photoisomerization of *cis* and *trans* piperylenes. This is verified, at least in part, by the existence of a temperature dependence for the photo *cis*→*trans* process.

On the basis of several pieces of evidence, it does not appear to be necessary to invoke cyclopropylmethylene biradicals as intermediates in the photo *cis-trans* isomerizations of 1,3-dienes.

---

25) E. Havinga, R. J. Dekock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1969).