magnetic contribution to the chemical shift vanishes. (2) The ^{33}S resonance in thiophene is found considerably lower than that of its tetrahydro analog. In general, resonances of aromatic, heteroaromatic, and other unsaturated compounds lie at lower field than their saturated analogs. For example, the ^{17}O resonance in furan is found 260 ppm below that of tetrahydrofuran,[24] the ^{13}C resonance in benzene is 101 ppm lower than that of cyclohexane,[26,27] and the ^{13}C resonances of unsaturated carbons in alkenes are found several tens of parts per million below those of the corresponding alkane carbons.[28]

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Conclusion

Although we have attempted to provide answers to the questions posed in the introduction, in essence our data offer only clues or partial answers. The broad ^{33}S resonances observed for most of the compounds examined indicate that, in general, measured chemical shifts are of low accuracy and that the possibility of differentiating between sulfur types in mixtures or in natural substances (such as coal) is an extremely remote one unless some means of removing quadrupole broadening is forthcoming or extremely high magnetic fields are employed.

Acknowledgments. The authors are indebted to Drs. F. R. Brown and R. G. Lett for stimulating discussions and thank one of the referees for his very helpful comments.

Spectroscopy of Phenylcyclopropanes and Phenylethanes. Unusual Emissions from Phenylcyclopropanes[1a]

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Abstract: At 77°K, all phenylcyclopropanes show a benzene-like absorption with a 0–0 band at 274–279 nm. The lesser substituted phenylcyclopropanes (mono-, 1,1-di-, and one 1,2-diphenyl) exhibit benzene-like fluorescence but no benzene-like or any other phosphorescence. The higher substituted phenylcyclopropanes (tri- and tetraphenyl) show no benzene-like fluorescence or phosphorescence but do show a short-lived (~7 msec), long wavelength (~580 nm) phosphorescence. The long wavelength phosphorescence is assigned as originating from a radical-like triplet state in which the C–CH$_2$–C bond angle is large (100–140°) and the cyclopropane bond connecting the carbon atoms to which the phenyl rings are attached is severely stretched. Mechanisms are given for the quenching of the benzene-like fluorescence and phosphorescence including the role of exciton interaction. A mechanism is given to account for the absence of the radical-like phosphorescence in lesser substituted phenylcyclopropanes. Spin–orbit coupling appears to be large between the radical-like singlets and triplets based on the short lifetime of the phosphorescence as well as its relatively high intensity and the apparent absence of a radical-like fluorescence. We believe an important source of the spin–orbit interaction is from first-order coupling involving one-center terms. The presence of the unusually low-energy radical-like triplet appears to be important in the triplet–triplet sensitized cis–trans isomerization of 1,2-diphenylcyclopropane with low-energy sensitizers. In addition either or both of the radical-like triplet and singlet states are the important excited states leading to direct photoisomerization and/or cycloelimination. The emission spectroscopic results of phenylethanes at 77°K are consistent with the existence of exciton interaction.

We have carried out a comprehensive study of the action of light upon some of the phenylcyclopropanes primarily at 77°K where both photochemical change and optical properties were monitored. Due to some unusual emission results and trends, a complementary study of the phenylethanes was also carried out. The lesser phenyl-substituted cyclopropanes exhibited only a benzene-like fluorescence whereas the more highly phenyl-substituted members exhibited only a very long wavelength (540–585 nm) phosphorescence (not benzene-like). Furthermore, this phosphorescence had a short lifetime (~7 msec). It was believed that exciton effects[2] might be contributing to the behavioral trend, and a study of the emission properties of the phenylethanes, which were expected to show an exciton effect, was undertaken. Results from the phenylethanes are used to provide a partial basis for interpretation of the results obtained from the phenylcyclopropanes.

Considerable evidence exists verifying thermal ring opening[3] of the cyclopropane ring, and the photochemistry of the cyclopropane ring system has been ex-

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(1) (a) All spectroscopy and photochemistry were done at the University of Houston and the synthesis of phenylcyclopropanes at the Louisiana State University, New Orleans; (b) University of Houston; (c) Louisiana State University.

(2) M. Kasha, H. R. Rawls, and M. Ashraf El-Bayoumi, *Pure Appl. Chem.*, 11, 371 (1965).

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tensively studied.[4–6] In addition, the low-temperature photochemistry and spectroscopy of the phenyloxiranes has been studied in detail.[7,8] The low-temperature studies (77°K) described in this paper, however, show that the cyclopropanes exhibit a complete lack of net photoproduct production except for the *cis*-1,2-diphenyl derivative. Furthermore, the low-energy (yellow) phosphorescence is assigned as originating in a π,π^* triplet of the phenylcyclopropanes which has appreciable diradical character.

Experimental Section

Most low-temperature work was done at 77°K in a rigid 3-methylpentane solution. The 3-MeP was purified by refluxing and distillation over sodium metal and passage through an alumina–silver nitrate column. The optical density of solutions in a 2-mm cell at 200 nm was about 0.1. Flat 2-mm cells as well as optical dewars were of Suprasil II quartz. Absorption spectra were taken on a Cary 15. Emission and excitation spectra were determined from an emission apparatus using a front face illumination and detection configuration.

Preparation and purification of the cyclopropanes are detailed individually as follows.

Phenylcyclopropane. The synthesis of phenylcyclopropane was achieved from cinnamaldehyde by the method described by Peterson and Skell.[9] Subsequent purification of the hydrocarbon after distillation (50° (5 mm)) was achieved by preparative glc on a glass column (2 m × 8 mm o.d.) packed with 60–80 mesh Chromosorb coated with silicone gum (SE–30, 10%) followed by molecular distillation.

cis- **and** *trans*-**1,2-Diphenylcyclopropane.** The isomeric 1,2-diphenylcyclopropanes were prepared by decomposition of 3,5-diphenyl-Δ^2-pyrazoline (that derived from benzalacetophenone) according to the method described by Beech, Turnbull, and Wilson.[10] Preparative separation and purification of the products was achieved efficiently on a glass column (2 m × 8 mm) coated with silicone gum (SE–30; 10%) or DC 550. The cis isomer eluted first and generally crystallized, and further purification of this isomer was achieved by recrystallization from pentane.

1,1-Diphenylcyclopropane. This hydrocarbon was prepared according to the procedure of Corey and Chaykovsky consisting of addition of 1,1-diphenylethylene to dimethyloxisulfonium methylide.[11] Separation of the desired cyclopropane from unreacted 1,1-diphenylethylene was achieved utilizing glc techniques and conditions identical with those described for phenylcyclopropane. A similar column with 20M as a liquid phase also may be employed effectively in the separation.

1,1,2-Triphenylcyclopropane. Treatment of styrene with diphenyldiazomethane at 90° according to the method reported by Griffin and coworkers gave 1,1,2-triphenylcyclopropane which was recrystallized from methanol to give a product with mp 49.5–50° (51%).[12]

1,1,2,2-Tetraphenylcyclopropane. Diphenyldiazomethane was decomposed thermally (300°) in the presence of 1,1-diphenylethylene utilizing the method described by Hodgkins and Hughes.[13] Separation of the product from residual starting material and byproducts was achieved by elution chromatography on alumina and final purification by recrystallization from ethanol, mp 166° (lit.[13] 165.5–166°).

Results

A. Phenylcyclopropanes. At 77°K in 3-MeP, no stable photochemical products were detected for any of phenylcyclopropanes except the *cis*-1,2-diphenyl derivative. Spectral results for the phenylcyclopropanes are summarized in Table I.

Table I. Optical Data on the Phenylcyclopropanes in Rigid 3-Methylpentane Glass at 77°K

Phenyl-cyclopropane	Absorption (0–0), nm	Fluorescence (0–0), nm	Phosphorescence max, nm (τ, msec)
Mono-	274	275	Absent
1,1-Di-	275	275	Absent
1,2-(*trans*)	277	Absent	540 (8.5 ± 0.5)
1,2-(*cis*)	274	274	560 (8.0 ± 1.0)
1,1,2-Tri-	277	Absent	585 (7.0 ± 0.5)
1,1,2,2-Tetra-	279	Absent	580 (6.9 ± 0.5)

Phenyl- and 1,1-diphenylcyclopropane showed an absorption and fluorescence emission very similar to toluene or ethyl benzene; that is, in 3-MeP at 77°K, both showed an absorption at ~274 nm (0–0) and an emission at ~275 nm (0–0). The vibronic envelopes were also similar in appearance even though in the monophenyl case the benzene-like fluorescence was partially obscured by an impurity (probably β-methylstyrene) present from the start. No phosphorescence of any type was observed in either case. Excitation spectra duplicated the absorption spectra of the compounds.

trans-1,2-Diphenylcyclopropane also showed a toluene-like absorption (0–0 at 276.8) but apparently did not fluoresce (an impurity whose fluorescence is very similar but not exactly that of β-methylstyrene[14] obscured much but not all of the region in which benzene fluorescence would occur). However, the trans derivative did show a long-lived asymmetrically shaped emission maximizing at 540 nm with a lifetime of 8.5 msec. The excitation spectra of this yellow emission reproduced the absorption spectrum of the parent compound.

Both 1,1,2-triphenyl- and 1,1,2,2-tetraphenylcyclopropane showed only a long-lived yellow emission peaking at 586 nm (τ = 7.0 ± 0.5 msec) and 578 nm (τ = 6.9 ± 0.5 msec), respectively. Although another weak emission was observed using the tetraphenylcyclopropane, the excitation spectrum did not reproduce the absorption spectrum of the cyclopropane compound. Excitation spectra of the yellow emissions duplicated the absorption of the parent compounds.

cis-1,2-Diphenylcyclopropane shows a fluorescence (0–0 at 274 nm) and a very weak emission centered at about 560 nm (τ = 8.0 ± 1.0 msec). The spectral results for this compound (representative of the phenylcyclopropane series) are presented in Figure 1a. The excitation spectrum duplicated the absorption spectrum. However, after prolonged 268-nm irradiation at 77°K in 3-MeP, net photochemistry was seen to occur. A product evolved which fluoresced (0–0 at 293.5 and with

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(14) Emission peaks of fluorescence of β-methylstyrene in 3–MeP at 77°K in nm: 292.5 (0–0), 299 (s), 302.0, 307.5, 317.5.

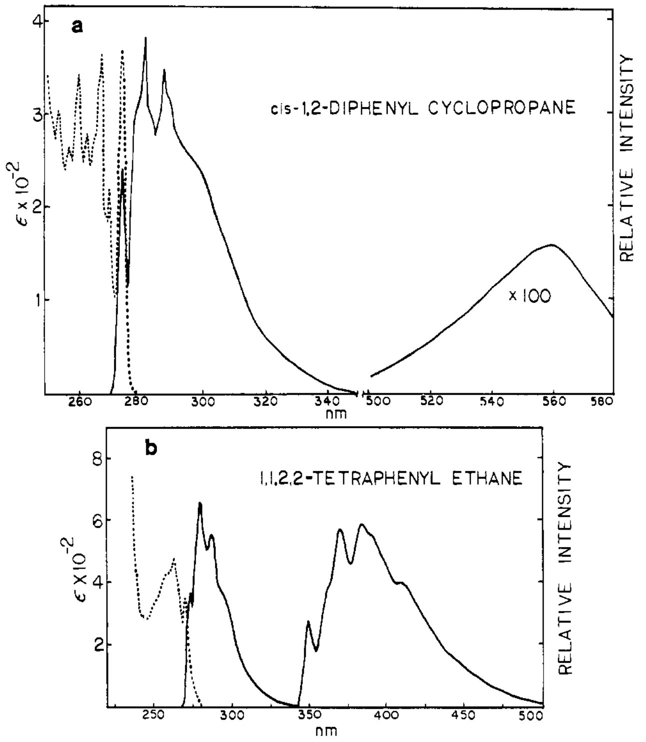

Figure 1. The absorption (·····) and emission (——) spectra of (a) *cis*-1,2-diphenylcyclopropane and (b) 1,1,2,2-tetraphenylethane in 3-methylpentane glass at 77°K.

a vibronic envelope nearly identical with β-methylstyrene)[14] and phosphoresced (0–0 at 361 nm and other bands at 367 (max) and 381 nm) with a lifetime of 7.7 sec. A new series of four or five bands also evolved between 483 and 535 nm (different runs produced slightly differing results) and is believed to originate from benzyl radical.[7,15,16] This emission disappeared almost immediately upon slow warming (*i.e.*, while the 3-MeP matrix was still macroscopically rigid), as did the phosphorescence maximizing at 367 nm. Additionally, in the rigid matrix a weak emission with peaks at 355, 376, 389, 399, 414, and 440 nm was observed. However, the excitation spectrum showed that the series actually consisted of two separate fluorescences. Monitoring those emissions at 355 and 376.5 nm generated identical excitation spectra with peaks at 351, 3.3, and 319 nm while the emissions at 389, 399, 414, and 440 nm were associated with an excitation spectrum peaking at 384, 377, and 361 nm. The higher energy emission (355 and 376 nm) disappeared almost immediately as the glass was warmed, while the longer wavelength emission (389, etc.) persisted much longer, finally disappearing near room temperature. It has previously been suggested elsewhere[7] that an emission very similar to one observed here (355 and 376.5 nm) originated from phenylcarbene. Upon warming and recooling to 77°K, the styrene like fluorescence (0–0 at 293.5 and the phosphorescence at 361 nm, etc.) persisted while the bands at 355, 376, and 483 nm, etc., failed to recur. The results on the disappearance of the two different sets of bands are consistent with these radical or carbene species dimerizing in fluid solution.[7]

Room-temperature photochemical studies were carried out on the *cis*-diphenyl isomer. In one case, just *cis*-1,2-diphenylcyclopropane was irradiated for 30 min with a 1-kW Xe lamp through a quartz–water filter and a Corning 9863 filter (cutoff at about 230 nm). A second identical run was performed except that *cis*-piperylene (~0.5 *M*) was added as a triplet quencher. In the absence of piperylene, all the original compound vanished with the formation of at least two new emitting compounds. One of these emissions was quite similar but not identical with that of β-methylstyrene (less similar to styrene or an α-methylstyrene),[17] and the other was a broad, structureless fluorescent emission maximizing at 441 nm. However, with piperylene present, not all of the cis compound was reacted and only the styrene-type emission evolved. Thus, since *cis*-piperylene exhibits nearly unit efficiency in collisionally deactivating triplet molecules,[18] the difference in the two experiments implies that the emission at 441 nm arises from a species photochemically generated exclusively from the triplet state. Furthermore, the styrene-like emission arises from a molecule produced photochemically at least in part from the lowest excited singlet state. We therefore conclude that, at least for the case of *cis*-1,2-diphenylcyclopropane at room temperature, photochemistry can occur in both the lowest excited singlet and triplet states.

We tried to sensitize the triplet state of the 1,1,2,2-tetraphenylcyclopropane at 77°K in 3–MeP. If it were assumed that the triplet level (0–0) lay above 28,600 cm^{-1} (as in tetraphenylethane and discussion below), then the sensitizer's triplet must lie above this and yet have its absorption below 35,700 cm^{-1}, the onset of the cyclopropane absorption. Pyrimidine seemed to fit the requirements; however, the results were negative and no sensitized phosphorescence was observed.

The direct excitation of 4-methyl-2-pentanone results in the production of propylene and acetone. The quantum yield ratio of the production of propylene without ($\phi_{\rm P}{}^0$) and with ($\phi_{\rm P}{}^{\rm Q}$) tetraphenylcyclopropane, $\phi_{\rm P}{}^0/\phi_{\rm P}{}^{\rm Q}$, is 1.26 ± 0.10 (0.02 *M* tetraphenylcyclopropane).[19] The quantum yield ratio of cis to trans isomerization of *cis*-piperylene in a mixture of the pentanone and *cis*-piperylene ($\phi^0{}_{\rm c\to t}$) and in the presence of tetraphenylcyclopropane ($\phi^{\rm Q}{}_{\rm c\to t}$), $\phi^0{}_{\rm c\to t}/\phi^{\rm Q}{}_{\rm c\to t}$, is 1.04 ± 0.10 (0.025 *M* *cis*-piperylene and 0.02 *M* tetraphenylcyclopropane).[19] Evaluation of the two quantum yield ratios indicates that under our concentration conditions, tetraphenylcyclopropane is quenching primarily the triplet state of the methylpentanone. In these experiments, the methylpentanone absorbed greater than 90% of the 3130-Å filtered exciting light from a Hg arc.[19] The tetraphenylcyclopropane contained an impurity, and the emission spectrum indicated it was tetraphenylethylene. We estimate the amount to be approximately 1% of the tetraphenylcyclopropane. We point this out since if the concentration of the impurity were to be 10% of the

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(17) Emission peaks of fluorescence of α-methylstyrene in 3-MeP at 77°K in nm: 292.3 (0–0), 297.1, 301.9, 307.0, 312 (s), 316.0.

(18) For example, P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 80 (1968).

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Table II. Optical Data on the Phenylethanes in Rigid 3-Methylpentane Solutions at 77°K

Structure	Absorption, 0–0, nm	Fluorescence, 0–0 (max), nm	Phosphorescence, 0–0 (max), nm	τ_{phos}, sec	$\phi_{\mathrm{P}}/\phi_{\mathrm{F}}$
Ph–C–C[a]	268	268 (282)	344 (366)	6.8 ± 0.2	1.06
Ph–C–C–Ph	268	268 (281)	343 (363)		1.35
$\mathrm{Ph_2}$–C–C	269	269.5 (276)	348 (368.5)	7.5 ± 0.2	1.56
$\mathrm{Ph_2}$–C–C–$\mathrm{Ph_2}$	270	270 (279)	349 (370)	7.0 ± 0.5	1.93

[a] Essentially identical with that of toluene; also see ref 33.

tetraphenylcyclopropane and if the triplet quenching efficiency of the impurity was equal to that of *cis*-piperylene, then quenching of the propylene production could be due to the impurity.

Based upon the long lifetime, the yellow (540–586 nm) emission obtained from the 1,2-diphenyl-, tri-, and tetraphenylcyclopropanes is assigned as a phosphorescence (also see following discussion).

No epr signal could be seen from irradiation of the tetraphenylcyclopropane with a 100-W Hg arc at 77°K.

B. Phenylethanes. Spectral results for the phenylethanes are summarized in Table II. All spectral observations were carried out at 77°K in a rigid 3-methylpentane (3-MeP) solution. A representative spectrum containing absorption and emission curves is given in Figure 1b for tetraphenylethane.

Discussion

A. Phenylcyclopropanes. Because of several complexities regarding the nature of and presence and absence of various kinds of emissions, we shall summarize our conclusions at the beginning. We shall develop the basis and justification for these conclusions following this summary.

(1) Based on the energy and intensity of the absorption spectra, excitation occurs to a benzene-like first excited π,π^* singlet state in all cases.

(2) The emission of three molecules with a 0–0 band at 274–275 nm is assigned as a fluorescence originating in the lowest benzene-like π,π^* singlet state based on the energy of the emission, the overlap with the first transition, and the similarity to benzene fluorescence (and alkylbenzenes).

(3) The unstructured emission of four molecules with maximum in the region 540–585 nm and lifetime of 7–8.5 msec is assigned as a phosphorescence. The phosphorescence originates from a triplet state in which the cyclopropane carbon–carbon bond between the phenyl groups is severely stretched and the cyclopropane C–$\mathrm{CH_2}$–C angle is large (100–140°). The phosphorescence is likely from a π,π^* triplet of a 90,90 conformer although the possibility of a 0,0 conformer cannot be eliminated.

A 90,90 conformer is one in which the plane of the carbon–hydrogen and carbon–phenyl bonds is essentially perpendicular to the plane of the cyclopropane carbon skeleton (as in the ground state). The 0,0 conformer is one in which the plane of the carbon–hydrogen and carbon–phenyl bonds lies essentially in the plane of the cyclopropane carbon skeleton.

The emitting triplet state has considerable diradical character on the basis of the presence or absence of phosphorescence as a function of the location and number of phenyl rings.

(4) Exciton interaction apparently occurs for polysubstituted phenylcyclopropane molecules based on a study of model phenylethanes and the quenching of the benzene-like fluorescence in the phenylcyclopropanes.

(5) Benzene-like fluorescence quenching in polysubstituted phenylcyclopropane molecules occurs *via* a combination of (a) the existence of a lowest lying forbidden singlet exciton state resulting from phenyl–phenyl interaction and (b) from a type of interstate crossing originating in the exciton benzene-like singlet state leading to a π,π^* singlet state of the phenylcyclopropanes in which the C–$\mathrm{CH_2}$–C bond angle is large (100–140°) and the cyclopropane C–C bond between the phenyl groups is severely stretched and has considerable diradical character [as in the triplet state(s) described in (3)].

(6) The benzene-like phosphorescence is totally quenched. The quenching arises from a combination of the mechanism described in (5b) which decreases the degree of occupancy of the benzene-like triplet and a type of interstate crossing between the benzene-like triplet and the radical-like triplet [of the type described in (3)]. Both of these lead to a radical-like phenylcyclopropane π,π^* triplet state of the type described in (3).

(7) No net photochemistry occurs at 77°K except for the *cis*-1,2-diphenylcyclopropane.

Phenylcyclopropane shows an absorption and fluorescence similar to toluene or ethylbenzene; however, no phosphorescence of any kind ($\phi_{\mathrm{P}} \leq 0.001$) was observed (Table II). Since in all other aspects of its spectroscopy, phenylcyclopropane is quite similar to ethylbenzene, one would expect the lowest benzene-like triplet and phosphorescence to occur near 345 nm (0–0 band). The fact that no emission was observed in this region verifies that quenching is occurring. Furthermore, since internal conversion does not quench phosphorescence in benzene or any other mono- or polyphenyl-substituted alkane (*vide infra*), the presence of quenching by some other mechanisms is a virtual certainty.

The 1,1-diphenylcyclopropane also behaves very much like ethylbenzene except that it like phenylcyclopropane shows no phosphorescence of any kind. This result once more suggests that some special quenching mechanisms exist.

cis-1,2-Diphenylcyclopropane responds in several ways after absorption of light. A benzene-like fluorescence is present but, in addition, a very weak phosphorescence also exists at 560 nm (Table II and Figure 1a). No phosphorescence exists in the spectral region where benzene, alkyl benzenes, or phenylethanes emit. The phosphorescence observed is at a much too low energy to be associated with a benzene-like phosphorescence and the lifetime is only 8 msec compared to 7 sec

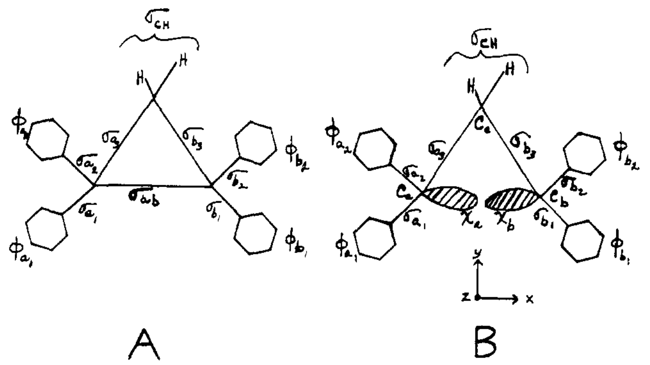

Figure 2. Structure of closed tetraphenylcyclopropane ground (A) and radical-like state (B). The phenyl rings a_1, b_1, a_2, and b_2 are not in the plane of the cyclopropane ring (twisted about σ_{a_1}, etc.) and $C_{a,b,c}$ identifies the carbon atoms.

for ethylbenzene (also benzene and phenylethanes). Also, recall that the *trans*-1,2-diphenyl- and tri- and tetraphenylcyclopropanes show no benzene-like fluorescence or phosphorescence but do have a short-lived, long wavelength phosphorescence (Table II). In view of the foregoing considerations, we are convinced that the observed phosphorescences have a very special origin. Upon slight warming above 77°K, irradiation no longer produces this low-energy emission.

Theoretical studies have been carried out on cyclopropane[20,21] and so-called open forms of cyclopropane.[22–26] Vacuum ultraviolet data and assignments are also available on cyclopropane.[20,21,27] In cyclopropane, two relatively intense $\sigma^* \leftarrow \sigma$ transitions occur at 70,000 and 83,000 cm^{-1}. Calculations[20] indicate only very small singlet–triplet splitting of 0.6 eV for any of nine excitations which is in sharp contrast to that for the π,π^* configuration for cyclopropene (over 4 eV).[20] Calculations[22] on the 0,0 form indicate a minimum exists in the ground-state singlet of cyclopropane at a C–C–C angle of ~110° and at ~110° for the triplet (no configuration interacting considered for the triplet). In the case of the 90,90 form, configuration interaction of two configurations indicates no minimum exists in the ground-state singlet at large angles.[22] This is also true when more extended configurational interaction is considered.[24] However, calculations with a variation in carbon–carbon lengths have not been done and could alter the results. Although a minimum does appear to be present in the triplet ground state of the 90,90 form[22] at a C–C–C angle of ~110°, configuration interaction results are not available.

Rotational energy barriers have been calculated[22] for the ground-state 0,0 form and 90,90 form with a C–C–C angle of 110°. For the 0,0 form the C–C rotational barriers in the singlet and triplet were 2.5 and <1 kcal/mol, respectively. In the case of the 90,90 form, the barriers were 1.5 and <1 kcal/mol for the singlet and triplet, respectively. However, considerations such as changes in C–C bond lengths, C–H angles, and orientation of terminal methylenes were not considered. It would not be surprising if the rotational barriers were in error by 1–3 kcal/mol.

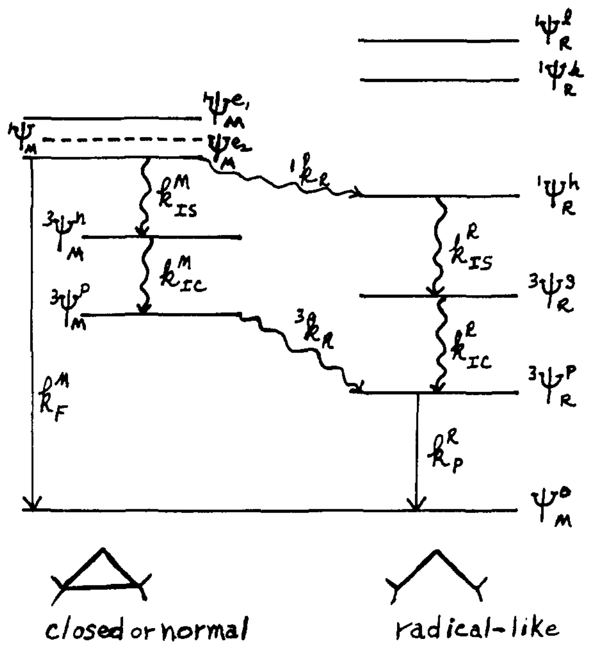

Figure 3. Energy level diagram for tetraphenylcyclopropane benzene-like (M) and radical-like (R) states. The states with superscript e_1 and e_2 are exciton states.

Calculations[25] also indicate a high degree (%) of π-diradical character in the ground-state 0,0 form at a C–CH$_2$–C angle of 120°; however, some difficulty exists in arriving at a precise definition of per cent diradical character. It also has been noted[25] that the greater the diradical character the less stable is the 0,0 open form.

In our case certain additional features are present compared with unsubstituted cyclopropane. In the first place, the presence of phenyl groups permits the existence of relatively low-lying benzene-like (and exciton) π,π^* states. Secondly, these same groups can interact with p-type atomic orbitals existent in the 90,-90 or 0,0 conformer form (*vide infra*). We shall call states resulting from such interaction radical-like molecule states. Thirdly, our experimental data show phosphorescence occurs only in those cases where the number and location of the phenyl substitution would stabilize a radical-like state (or molecule). This observation is therefore consistent with a radical-like nature for the emitting triplet and is in agreement with the radical-like nature calculated for the ground state 0,0 and for 90,90 conformers. Fourthly, different coupling(s) will be effective between the radical-like singlet and triplet π,π^* states than is normally the case between usual π,π^* states of different multiplicity (*vide infra*). We also believe the latter is true for the phenylcyclopropane molecules.

We believe it is most clear and instructive to first discuss the tetraphenyl case. The discussion for the triphenyl and diphenyl cases would be essentially parallel. Figure 2 presents a diagram of the tetraphenylcyclopropane closed or normal, M for molecule, form as well as that for the radical-like molecule, R for radical.

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Figure 3 presents an energy level diagram and mechanistic paths. The $\psi_M(\pi,\pi^*)$ state results from excitation of the type

$$\Psi_M(\pi_i,\pi_j^*) \equiv \Psi_M(\psi_{M_i},\psi_{M_j}^*) \tag{1}$$

where

$$\Psi_M = \lambda_A{}^M\Phi_A + \lambda_B{}^M\Phi_B \tag{2}$$

and where, for example

$$\Phi_A = C_1{}^A\Phi_{a_1}' + C_2{}^A\Phi_{a_2}' \tag{3}$$

and where, for example

$$\Phi_{a_1}' = C_1{}^{a_1}\phi_{a_1} + C_2{}^{a_1}\sigma_{ab} + C_3{}^{a_1}\sigma_{b_3} + C_4{}^{a_1}\sigma_{CH}C_5{}^{a_1}\sigma_{a_3} + \ldots \tag{4}$$

The absorption and fluorescence spectra indicate that the lowest energy transition is benzene-like. Thus in the foregoing equations Ψ_{M_i} and $\psi_{M_j}{}^*$ are benzene-like molecular orbitals and $C_1{}^{a_1}$ is the dominant coefficient in Φ_{a_1}' and similar equations. The $^1\Psi_M{}^{e_1}(\pi,\pi^*)$ and $^1\Psi_M{}^{e_2}(\pi,\pi^*)$ states result from exciton interaction of the $^1B_{2u}$ benzene states of the phenyl substituents (Figure 3). Justification for exciton interaction is discussed more later and is further substantiated by study of model phenylethanes (*vide infra*).

The radical-like states, ψ_R, are constructed as follows

$$\Psi_R(\pi_i,\pi_j^*) \equiv \Psi_R(\psi_{R_i}\psi_{R_j}^*) \tag{5}$$

where

$$\Psi_R = \lambda_A{}^R\Phi_A + \lambda_B{}^R\Phi_B \tag{6}$$

and where, for example

$$\Phi_A = C_1{}^A\Phi_{a_1}' + C_2{}^A\Phi_{a_2}' \tag{7}$$

and where, for example

$$\Phi_{a_1}' = C_1{}^{a_1}\phi_{a_1} + C_2{}^{a_1}\chi_a + C_3{}^{a_1}\sigma_{b_3} + C_4{}^{a_1}\sigma_{CH} + \ldots \tag{8}$$

It is assumed that the plane of the phenyl rings a_1, b_1, a_2, and b_2 are not in the plane of the cyclopropane ring (twisted about σ_{a_1}, etc.) for both M and R states and that χ_a and χ_b are p-type atomic orbitals (overlap small but finite).

It is necessary to explain (1) the unusually low energy, (2) the unusually short lifetime, and (3) the relatively high quantum yield of the observed phosphorescence, (4) the absence of benzene-like fluorescence for polyphenyl 1,2-substituted cyclopropanes present, for example, in the monosubstituted case, and (5) the absence of benzene-like phosphorescence. The low energy of the radical-like triplet state can be understood by virtue of the coupled phenyl π systems as represented by eq 6 ($\lambda_A{}^R$ and $\lambda_B{}^R$ are comparable in magnitude). The quenching of the benzene-like fluorescence results from a combination of intrastate crossing from $^1\psi_M$ to the radical-like $^1\psi_R(\pi,\pi^*)$ state, ^1k_R, and through relatively increased intersystem crossing to the benzene-like triplet, $^3\psi_M{}^P$, Figure 3. These both occur because of the existence of a lower forbidden exciton-type $\psi_M{}^{e_1}(\pi,\pi^*)$ state. The latter situation results in τ_F becoming longer and the other two processes becoming dominant. More discussion concerning this point will be given shortly.

The rate constant for formation of the radical-like triplet state form the benzene-like triplet state, ^3k_R, is of sufficient magnitude to totally quench the $^3\psi_M{}^P(\pi,\pi^*)$ benzene-like lowest triplet since the lifetime of this latter state is expected to be very long (>1 sec) (Figure 3). It is possible that the rate constant for formation of the radical-like singlet state from the benzene-like singlet state, ^1k_R, is of sufficient magnitude to totally quench fluorescence and intersystem crossing and thus the benzene-like phosphorescence because of a vanishingly small occupation of the benzene-like lowest triplet (phosphorescent) state, $^3\psi_M{}^P(\pi,\pi^*)$. One or both processes just described provide a potential quantum yield of eventual occupation of the lowest radical-like triplet state $^3\psi_R{}^P(\pi,\pi^*)$ of ~0.5. In view of the intense phosphorescence from the radical-like triplet $^3\psi_R{}^P(\pi,\pi^*)$, it is apparent that little internal conversion occurs. More discussion concerning the quenching of the benzene-like phosphorescence will be given shortly.

The important remaining concerns are those relating to the unusually short lifetime for a π,π^*-type phosphorescence and the dominance of intersystem crossing from $^1\psi_R{}^h(\pi,\pi^*)$ to $^3\psi_R{}^P(\pi,\pi^*)$, Figure 3. The latter are unusual between π,π^* states. By dominance we mean that no emission apparently is observable from $^1\psi_R(\pi,\pi^*)$ and the radical-like phosphorescence is intense. The following development assumes crossing occurs to a π,π^* triplet state intermediate to $^1\psi_R{}^h(\pi,\pi^*)$ and the emitting triplet $^3\psi_R{}^P(\pi,\pi^*)$. The important point is the determination of whether one-center spin–orbit coupling matrix elements exist between (π,π^*) singlets and triplets in the radical-like molecule. If one-center terms exist, crossing to an intermediate triplet may not be a necessary requirement. The intersystem crossing yield to first-order depends on (Figure 3)

$$\langle {}^1\Psi_R{}^h(\pi,\pi^*)|H_{SO}|{}^3\Psi_R{}^g(\pi,\pi^*)\rangle \tag{9}$$

neglecting spin-vibronic contributions. Expanding this in terms as in eq 5–8 gives

$$\lambda_{R_A}{}^1\lambda_{R_B}{}^n\langle\Phi_a|\zeta'l|\Phi_B\rangle + \lambda_{R_B}{}^1\lambda_{R_A}{}^n\langle\Phi_B|\zeta'l|\Phi_A\rangle + \ldots \tag{10}$$

and

$$\langle\Phi_{a_1}'|\zeta'l|\Phi_{b_1}'\rangle + \langle\Phi_{a_1}'|\zeta'l|\Phi_{b_2}'\rangle + \langle\Phi_{a_2}'|\zeta'l|\Phi_{b_1}'\rangle + \ldots \tag{11}$$

where coefficients have been omitted and

$$\langle\chi_a|\zeta'l|\sigma_{a_3}\rangle + \langle\chi_b|\zeta'l|\sigma_{b_3}) + \langle\chi_a|\zeta'l|\sigma_{a_1}\rangle + \langle\sigma_{CH}|\zeta'|\sigma_{a_3}\rangle + \ldots \tag{12}$$

From (12) one-center integrals arise of the type

$$\begin{gathered}\langle P_{x\cdot C_a}|\zeta'l|P_{y\cdot C_a}\rangle \rightarrow \zeta' \\ \langle P_{x\cdot C_b}|\zeta'l|P_{y\cdot C_b}\rangle \rightarrow \zeta'\end{gathered} \tag{13}$$

and the sum in eq 12 does not equal 0. Although we cannot and do not wish to exclude second-order couplings, spin–orbit-vibronic, we believe first-order spin–orbit coupling is important because of the presence of the one-center terms.

The short phosphorescent lifetime arises principally because of first-order direct spin–orbit coupling of $^1\psi_R{}^h(\pi,\pi^*)$ and $^3\psi_R{}^P(\pi,\pi^*)$ or higher singlets as $^1\psi_R{}^k,{}^1\psi_R{}^l$ with the $^3\psi_R{}^P(\pi,\pi^*)$ state, Figure 3. Again, we do not wish to exclude second-order couplings but believe first-order spin–orbit coupling is an important source of the interaction.

Earlier we mentioned the existence of exciton states in the tetraphenyl case. Evidence for this is based on spectral results of model phenylethanes, which we shall discuss shortly, and the ultimate total quenching of the benzene-like fluorescence in the more highly substituted phenylcyclopropane cases. Furthermore, in the case of the phenylcyclopropane molecules, M, intersystem crossing will depend in first order on

$$\langle {}^1\Psi_{\mathrm{M}}{}^{\mathrm{e}1}(\pi,\pi^*)|H_{\mathrm{SO}}|{}^3\Psi_{\mathrm{M}}{}^{\mathrm{n}}(\pi,\pi^*)\rangle$$

neglecting spin-vibronic interaction. This can be expanded using eq 1–4 in a manner similar to that for eq 10–13 above for the radical-like molecule giving terms, for example, as

$$\langle\sigma_{\mathrm{ab}}|\zeta' l|\sigma_{\mathrm{a}_3}\rangle + \langle\sigma_{\mathrm{ab}}|\zeta' l|\sigma_{\mathrm{b}_3}\rangle + \langle\sigma_{\mathrm{CH}}|\zeta' l|\sigma_{\mathrm{a}_3}\rangle + \langle\sigma_{\mathrm{ab}}|\zeta' l|\sigma_{\mathrm{a}_2}\rangle + \ldots \neq 0$$

The general state coupling schemes for any of the other *phenylcyclopropane radical-like molecules* should be similar to that described above. The wave functions will vary of course in the nature and number of terms. The absence of the radical-like molecule phosphorescence for the monophenyl- and 1,1-diphenylcyclopropanes principally occurs we believe because the lifetime of the triplet radical to closure to the normal cyclopropane in these cases is short compared with emission lifetime. Thus the phosphorescence would be quenched. Presumably the closure would occur by internal conversion to a distorted ground-state singlet of the cyclopropane (*vide infra*). It is also possible that the radical-like molecule state is not formed in these cases, but we consider this quite unlikely. We reach this last conclusion in part based on the presence of benzene-like fluorescence and the total quenching of the benzene-like phosphorescence, the latter of which would not be expected in the absence of a highly competing process leading to radical-like molecule triplet state formation. Also, it is expected that the stability of a radical-like molecule would be very short in the cases where one of the carbon atoms has only H atoms.

Exciton interaction is not expected in the monophenylcyclopropane case. Consequently, the rate constant for fluorescence is sufficiently great that intersystem crossing to a benzene-like triplet and formation of the radical-like singlet ${}^1\psi_{\mathrm{R}}{}^{\mathrm{h}}(\pi,\pi^*)$ (Figure 3) do not quench fluorescence. This would indicate that ${}^1k_{\mathrm{R}}$ is $\sim 10^8$–10^8 sec^{-1} in this case, which is also the magnitude expected for $k_{\mathrm{IS}}{}^{\mathrm{M}}$ and $k_{\mathrm{F}}{}^{\mathrm{M}}$. In the presence of exciton interaction, the expected decrease in $k_{\mathrm{F}}{}^{\mathrm{M}}$ contributes to the quenching of the benzene-like fluorescence because of a relative increase in both $k_{\mathrm{IS}}{}^{\mathrm{M}}$ and ${}^1k_{\mathrm{R}}$ compared with $k_{\mathrm{F}}{}^{\mathrm{M}}$ (Figure 3). The latter situation is apparent for the tetraphenyl-, triphenyl-, and one of the 1,2-diphenylcyclopropanes. We believe it is necessary to postulate formation of the radical-like ${}^1\psi_{\mathrm{R}}{}^{\mathrm{h}}(\pi,\pi^*)$ state from a benzene-like singlet (Figure 3). The reason is that the benzene-like fluorescence becomes totally quenched with an increase in the number of phenyl groups (two, three, or four groups), whereas in the model phenylethanes, this is not true. We see no obvious reason why the intersystem crossing rate in the more highly substituted phenylcyclopropanes (two, three, and four groups) should increase to such a significantly greater extent than in the phenylethanes as to be totally the cause of the quenching of the benzene-like fluorescence (of the polyphenyl 1,2-substituted cyclopropanes).

The benzene-like phosphorescence is quenched in every phenylcyclopropane derivative. Based on the presence of benzene-like fluorescence in the monophenyl, 1,1-diphenyl and *cis*-1,2-diphenyl cases, the presence of benzene-like fluorescence and phosphorescence in alkylbenzenes and all model phenylethanes, we believe that the benzene-like triplet should be occupied. However, benzene-like phosphorescence is quenched because ${}^3k_{\mathrm{R}}$ is significantly greater than that of the phosphorescence rate constant, $k_{\mathrm{P}}{}^{\mathrm{M}}$ (Figure 3) (recall particularly in the case of the 1,1-diphenyl derivative where some exciton interaction should exist and thereby $k_{\mathrm{IS}}{}^{\mathrm{M}}$ relatively increased, benzene-like fluorescence still occurs but benzene-like phosphorescence is quenched). We believe a parallel situation exists for the other cases regarding occupation and quenching of the benzene-like triplet state with the additional possibility of a reduced benzene-like triplet occupation because of the magnitude of ${}^1k_{\mathrm{R}}$ (Figure 3). It is not possible to quantitatively evaluate the relative importance of the two mechanisms proposed for quenching of the benzene-like phosphorescence: that is, formation of the radical-like singlet from the benzene-like singlet (${}^1k_{\mathrm{R}}$) and formation of the radical-like triplet from the benzene-like triplet (${}^3k_{\mathrm{R}}$). We only wish to say we believe that there are valid reasons (*vide supra*) to presume the benzene-like triplet must be occupied but that the expected phosphorescence is totally quenched because the relative magnitude of ${}^3k_{\mathrm{R}} \gg k_{\mathrm{P}}{}^{\mathrm{M}}$ (giving the radical-like triplet state).

We believe that the radical-like phosphorescence, vertical transition, occurs to a highly distorted phenylcyclopropane singlet ground state with a geometry essentially the same as that in the excited triplet state. Immediately following emission, vibrational relaxation occurs carrying the molecule to the closed or normal ground state (Figure 2A).

Recall the lifetime of the phosphorescence from the radical-like triplet state is remarkably constant and independent of the number of phenyl groups. We believe, therefore, that the intrinsic lifetime of the radical-like phosphorescence is $\sim$7.5 msec. The absence of radical-like phosphorescence in two cases indicates the lifetime of the radical-like molecules with phenyl group(s) only on one carbon atom is $<10^{-4}$ sec.

O'Connell, Martin, and Lis[28] have also studied the emission properties of some substituted cyclopropanes of which one was common to our investigation, phenylcyclopropane. Fluorescence and phosphorescence were reported to occur for the phenylcyclopropane although no wavelengths were given. The inference was that they were similar in spectral location to *n*-propylbenzene. This fluorescence result would then be in general agreement with our data; however, we observed no benzene-like or any other phosphorescence for the monophenyl case. They conclude that ring opening can, in some cases, quench emissions.

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(28) E. J. O'Connell, J. G. Martin, and J. T. Lis, *Chem. Commun.*, 95 (1970).

The observation has been made[29,30] that the trans → cis isomerization for *trans*-1,2-diphenylcyclopropane could be sensitized by triplet–triplet energy transfer from donor compounds whose triplet lay well below 29,470 cm^{-1} which is the location of the benzene triplet. For example, in 2-acetonaphthane the lowest triplet is at approximately 20,800 cm^{-1}.[31] In view of the results herein reported, we believe the triplet state involved in the acceptor *trans*-1,2-diphenylcyclopropane is the one located at approximately 540 nm (18,513 cm^{-1}, 53 kcal/mol). Of course the latter energy refers to the phosphorescence maximum, and the 0 level of the triplet state can only be estimated to be about 20,400 cm^{-1} above the 0 level of the ground state. Furthermore, in view of the great geometrical distortion of the phenylcyclopropane radical-like triplet state compared to the normal ground state, we would expect energy transfer to be relatively inefficient.

In addition to the foregoing, data are reported herein (*vide supra*) regarding the quenching of propylene production from 4-methyl-2-pentanone by tetraphenylcyclopropane. The results indicate that the latter cyclopropane can quench triplet states below those of the benzene triplet.

cis- and *trans*-1,2-diphenylcyclopropanes undergo photointerconversion, and these as well as other phenylcyclopropanes undergo photocycloelimination to form phenylcarbenes (at room temperature).[32] It is apparent that either or both of the radical-like triplet and singlet states discussed herein (*vide supra*) are the excited states having the structural features leading to isomerization and/or cycloelimination.

B. Phenylethanes. The observation that intramolecular exciton effects among phenyl rings may influence the emission properties of molecules was first made by Kasha, *et al.*[2a] They interpreted the increase in the phosphorescence to fluorescence ratio occurring in three phenylmethanes as a function of the number of phenyl rings to be the result of exciton interaction. Similar but smaller effects might be expected for the phenylcyclopropanes. However, such direct observations were not immediately possible for primarily two reasons. First, no benzene-like phosphorescence is present for any of the phenylcyclopropanes. Secondly, the benzene-like fluorescence in three derivatives is totally quenched. Hence, a study of model phenylethanes was undertaken to examine whether exciton effects were present in these types of systems and to provide a further basis for understanding of the emission spectroscopy of the phenylcyclopropanes.

The spectra (absorption and emission) of the phenylethanes were basically benzenoid in character (Table I and Figure 1b). The ratio of phosphorescence to fluorescence (ϕ_P/ϕ_F) was 1.06 for toluene or ethylbenzene.[33] If we assume that the small splittings of an exciton nature do not affect the rate of internal conversion to the ground state or introduce new photochemical pathways for deexcitation of the lowest excited state, then the change in the ϕ_P/ϕ_F ratio could reflect a relative decrease in the rate constant for fluorescence. Both of the assumptions should be valid since the exciton splitting is small and no photochemistry was observed for the phenylethanes. Given that the polarization of the $S_1 \leftarrow S_0$ is short axis as in toluene (the transition derived from the $^1B_{2u}$ band in benzene), exciton interaction in polyphenylethanes will result in exciton states of which the lower energy member will be forbidden. The existence of an optically forbidden exciton state as the lowest state would decrease the rate constant of the fluorescence emission and allow for a greater degree of intersystem crossing. The exciton effect for a triplet state is negligible because of the very small value of the $T \leftarrow S_0$ transition moment, and, therefore, little change is expected in the rate constant for phosphorescence.

Similar effects to those found in the phenylmethanes[1b] were observed in the phenylethanes (Table I). From ethylbenzene to 1,1-diphenylethane, ϕ_P/ϕ_F increases from 1.06 to 1.55, an increase of 46%. In the case of 1,2-diphenylethane where the greater separation of the phenyl rings should decrease the exciton effects, an increase of ϕ_P/ϕ_F of 28% was observed (1.06 → 1.35). Where both effects are present (1,1,2,2-tetraphenylethane), there is an overall increase of ϕ_P/ϕ_F of 85% relative to toluene. The phosphorescence lifetimes remained essentially identical for all phenylethanes (Table I).

Although the foregoing results for the phenylethanes are consistent with exciton interaction being responsible for the change in ϕ_P/ϕ_F, it is not a proof of that fact.

Conclusion and Summary

The emission spectroscopy of the phenylcyclopropanes is complicated to interpret. We believe the interpretation as given represents the best possible analysis of which the following is a summary.

The lesser substituted phenylcyclopropanes (mono-, 1,1-di-, and one 1,2-diphenyl) exhibit benzene-like fluorescence but no benzene-like or any other phosphorescence. The higher substituted phenylcyclopropanes (tri- and tetraphenyl) show no benzene-like fluorescence or phosphorescence but do show a short-lived (~7 msec), long wavelength (~580 nm) phosphorescence. The long wavelength phosphorescence is assigned as originating from a radical-like triplet state in which the C–CH_2–C bond angle is large (100–140°) and the cyclopropane bond connecting the carbon atoms to which the phenyl rings are attached is severely stretched. We believe that the benzene-like fluorescence is quenched through (1) a combination of interstate crossing to a radical-like excited singlet state (with a geometry as that described above for the radical-like triplet state) and (2) increased intersystem crossing to the benzene-like triplet. Exciton interaction plays a role in both of these. We believe the benzene-like phosphorescence is quenched *via* interstate crossing from the benzene-like triplet to a radical-like triplet state (of the type described above) and through reduced intersystem crossing to the benzene-like triplet state. The radical-like phosphorescence is absent in the mono- and 1,1-diphenylcyclopropanes because the lifetime of the radical-like triplet to closure to the normal cyclopropane *via* internal conversion is short

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(29) G. S. Hammond, P. Wyatt, C. D. Deboer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964).

(30) G. S. Hammond and R. S. Cole, *ibid.*, **87**, 3256 (1965).

(31) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley, New York, N. Y., 1969, p 158.

(32) G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1971).

(33) Kasha, *et al.*,[2a] report a ratio of 0.94 while a value of 1.06 was obtained in this laboratory.

compared to the emission lifetime. Spin–orbit coupling appears to be large between the radical-like singlets and triplets based on the short lifetime of the phosphorescence as well as its relatively high intensity and the apparent absence of a radical-like fluorescence. We believe an important source of the spin–orbit interaction is from first-order coupling (one-center terms).

The presence of the unusually low-energy radical-like triplet appears to be important in the triplet–triplet sensitized cis–trans isomerization of 1,2-diphenylcyclopropane with low energy sensitizers. In addition either or both of the radical-like triplet and singlet states are the important excited states leading to direct photoisomerization and/or cycloelimination.

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Vinylcyclopropane and Vinylcyclobutane

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Abstract: We have applied single determinant *ab initio* molecular orbital theory to the description of internal rotation in vinylcyclopropane and vinylcyclobutane. Using the minimal STO-3G basis we find the two molecules to be most stable in their s-trans forms but also predict both to possess flat secondary s-cis and gauche minima. Further investigation on vinylcyclopropane with the extended 4-31G basis set confirms the gauche minimum but places doubt on the stability of the s-cis structure. Substitution on the vinyl group in vinylcyclopropane by π-electron donors at the 2 carbon deepens the gauche minimum, while equivalent substitution one position removed has the opposite effect. Substitution by π-electron acceptors reverses the trend. These effects are readily accounted for by a simple one-electron model and are consistent with available experimental information on related systems. Small, but significant substituent effects are found on the relative energies of the vinylcyclobutane conformers. Here 2 substitution by either π acceptors or π donors destabilizes the gauche structure relative to the other two. The 1 substitution has little effect.

Compounds involving small rings have long held a special place in chemistry, in that they exhibit properties intermediate between systems which are formally saturated and those which contain some degree of unsaturation. Perhaps on account of their pecularity they have received constant and thorough attention from experimentalists and theorists alike but still in all several important questions remain unambiguously answered. Most of these stem from our present lack of knowledge as to the exact extent to which the formally saturated small ring compounds behave as if they were unsaturated. Such quantitative information should, in principle, be accessible by thermochemical and structural measurements, but up till now these experiments have either been impossible to perform or have led to ambiguous findings.[2] Our aim in this paper is to consider the first two members of the vinylcycloalkane family and to investigate theoretically both the conformational preferences of these molecules and the degree of interaction between the vinyl and cycloalkyl groups. We shall accomplish this by a straightforward application of *ab initio* molecular orbital theory, using our previously developed STO-3G[3a] and 4-31G[3b] basis sets. These have already met with considerable success in problems of potentials to internal rotation for a number of simple polyatomics.[4–6]

Methods

Standard single determinant molecular orbital theory is used throughout. We employ two different sets of basis functions in this study. The first closely simulates a minimal set of Slater-type orbitals (STO's) in that each STO is least-squares fitted to a sum of three Gaussians. The resulting functions, termed STO-3G,[3a] have been uniformly rescaled to be adequate for use in molecular calculations. In addition, we have recalculated several points on the potential surface of vinylcyclopropane using the extended 4-31G basis.[3b] Here atomic inner shells are each described by a single function written in terms of four Gaussians, while the valence shell is split into inner (three Gaussian) and outer (one Gaussian) parts. The Gaussian expansions, originally determined as energy optimum for the atom, have been rescaled. All calculations have been made with the GAUSSIAN 70 series of programs.[7]

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(1) (a) National Science Foundation Postdoctoral Fellow, 1971–1972. (b) The laboratoire de Chimie Théorique is also part of the Laboratoire de Physico-Chimie des Rayonnements, associated with the CNRS.

(2) For a good example of the uncertainty in the experimental spectroscopic interpretation of molecules containing small rings, see G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, 5, 167 (1970).

(3) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, 54, 724 (1971).

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(5) L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, 94, 2371 (1972).

(6) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, in press.

(7) GAUSSIAN 70, a series of programs designed to perform *ab initio* molecular orbital calculations on organic molecules: W. J. Hehre, W. A. Lathan, and J. A. Pople, to be submitted to the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind. Typical times for a single calculation on the molecules discussed in this paper are as follows (Univac 1108 computer): vinylcyclopropane,