Conformational Changes Involved in the Singlet–Triplet Transitions of Biphenyl[1]

Peter J. Wagner

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan. *Received November 4, 1966*

Abstract: The lowest energy band in the T* ← S absorption spectrum of biphenyl in benzene solution appears at 75.5 kcal. Naphthalene and conjugated dienes are 2.5 times more effective than biphenyl at quenching triplet butyrophenone and at least 20 times more effective than biphenyl at quenching triplet benzophenone. The actual quenching efficiency of biphenyl decreases with increasing benzophenone concentration because of reversible energy transfer. From these absorption and quenching data, plus phosphorescence data in the literature, it is concluded that neither the highest energy band in the phosphorescence spectrum at 65.5 kcal nor the lowest energy band in the solution T* ← S absorption spectrum at 75.5 kcal represents the true T* ↔ S 0–0 transition of biphenyl, which occurs around 69.5 kcal and is a nonspectroscopic transition between a twisted ground state and a triplet state of grossly different geometry. Evidence that triplet biphenyl prefers to be planar is presented and discussed.

In recent measurements of the phosphorescence spectrum of biphenyl in frozen glasses, the highest energy band has been located at 65.5 kcal and assigned as the T* → S 0–0 transition.[2] If the actual energy difference between the lowest vibrational levels of the ground and first triplet states were 65.5 kcal, biphenyl ought to quench higher energy (>68 kcal) ketone triplets at close to the diffusion-controlled rate in solution.[3–5] Since biphenyl absorbs only negligibly at 3130 A and is not known to undergo any photochemical changes, it seemed that it might be a choice quencher for use in studies of the triplet-state photochemistry of ketones. The work to be described grew out of a test of this assumption.

Results

Quenching of Butyrophenone Photoelimination. Biphenyl and several other aromatic and olefinic compounds with low-lying triplet states were used to quench type-II photoelimination of butyrophenone, whereby the excited molecule splits into ethylene and acetophenone. This reaction has been shown to proceed exclusively from the triplet state of the ketone.[6,7] Pyrex tubes containing benzene solutions 0.20 *M* in ketone, 0.005 *M* in *n*-tetradecane as internal standard, and containing various concentrations of the different quenchers were degassed, sealed *in vacuo*, and irradiated in parallel such that each sample absorbed the same intensity of 3130- or 3660-A radiation. The amount of acetophenone formed in each tube was then determined by glpc analysis. The highest conversion, in samples with no quencher, was 6%. Stern–Volmer plots, such as exemplified in Figure 1, were linear for each quencher, their slopes yielding the $k_q\tau$ values listed in Table I. Since the lifetime of triplet butyrophenone, τ, is the same regardless of quencher, it is apparent that biphenyl is less efficient a quencher by a factor of 0.40 than are the other compounds studied, all of which are commonly assumed to be "diffusion-controlled" quenchers. The fact that the quenching efficiency of naphthalene appeared slightly higher than that of the others probably is not significant, since acetophenone and naphthalene were not completely separated under the analytical conditions employed, and a small systematic error may readily have been introduced.

Table I. Efficiencies of Various Compounds at Quenching Photoelimination of Butyrophenone

Compound	E_T[a]	Wavelength, A	$k_q\tau$, M^{-1}
1,3-Pentadiene	59[b]	3130	670
2,5-Dimethyl-2,4-hexadiene	~58[b]	3130	640
Biphenyl	~69.5[c]	3130	275
Biphenyl		3660	276
Naphthalene	60.9[d]	3660	750
trans-Stilbene	~50[e]	3660	654
cis-Stilbene	58[e]	3660	665

[a] Triplet excitation energy, in kcal. [b] Reference 11. [c] Estimated in this work. [d] Reference 12. [e] Reference 13.

Quenching of Propiophenone Photoreduction. Isopropyl alcohol solutions 0.10 *M* in propiophenone and containing various concentrations (0–0.012 *M*) of naphthalene or biphenyl were degassed and irradiated in parallel in sealed Exax tubes at 3660 A. The disappearance of propiophenone was monitored by ultraviolet analysis. Again Stern–Volmer plots were linear and yielded slopes equal to 204 and 136 M^{-1} for naphthalene and biphenyl, respectively. Cohen has reported a $k_q\tau$ value of ~170 M^{-1} for the acetophenone–isopropyl alcohol–naphthalene system.[8]

Quenching of Benzophenone Photoreduction. Biphenyl and several other compounds were employed to quench the photoreduction of benzophenone by benz-

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[1] Triplet Energy Transfer. I. Presented in part at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

[2] (a) E. Clar and M. Zander, *Chem. Ber.*, **89**, 749 (1956); (b) Y. Kanda, R. Shimeda, and Y. Sakai, *Spectrochim. Acta*, **17**, 1 (1961); (c) V. Trusov and P. Teplyakov, *Opt. i Spektroskopiya*, **16**, 52 (1964); *Opt. Spectry.* (USSR), **16**, 27 (1964).

[3] K. Sandros and H. J. L. Bäckström, *Acta Chem. Scand.*, **16**, 956 (1962).

[4] G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A264**, 1 (1961).

[5] W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

[6] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

[7] E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966).

[8] S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

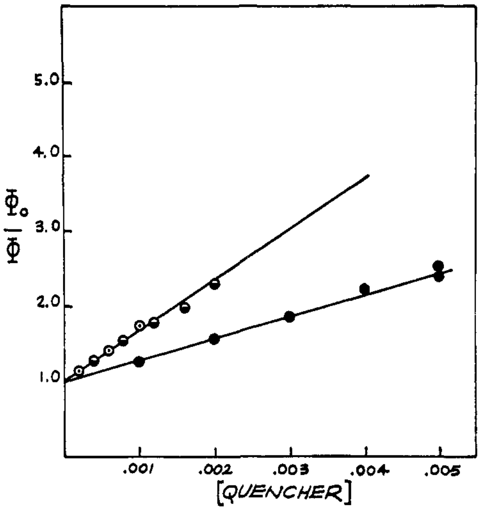

Figure 1. Stern–Volmer plots for quenching of butyrophenone photoelimination: ⊙, *cis*-stilbene; ◒, 2,5-dimethyl-2,4-hexadiene; ●, biphenyl.

hydrol in benzene solution.[9,10] Degassed, sealed Exax tubes containing 0.050 *M* benzophenone, 0.20 *M* benzhydrol, and various concentrations of the quencher were irradiated in parallel at 3660 A. Relative quantum yields for disappearance of benzophenone were measured by ultraviolet analysis. Stern–Volmer plots, such as exemplified in Figure 2, were linear with the slopes listed in Table II. Tables I and II both list literature values[11–13] for the triplet energies of the various quenchers.

Table II. Efficiencies of Various Compounds at Quenching Photoreduction of Benzophenone[a] by 0.20 *M* Benzhydrol

Compound	E_T[b]	S[c]
Naphthalene	60.9[d]	2470
2,5-Dimethyl-2,4-hexadiene	~58[e]	2660
Triphenylene	66.6[d]	360
Fluorene	67.6[d]	63[f]
Biphenyl	~69.5[g]	17
Biphenyl[h]	~69.5[g]	35
Biphenyl[i]	~69.5[g]	80
o-Fluorobiphenyl[j]	>69.5[g]	4.9
o-Chlorobiphenyl[j]	>69.5[g]	0.9

[a] Originally 0.050 *M* unless otherwise noted. [b] Triplet excitation energy in kcal. [c] Slope of Stern–Volmer plot. [d] Reference 12. [e] Reference 11. [f] Extrapolated to zero fluorene concentration. [g] Estimated in this work. [h] 0.020 *M* benzophenone. [i] 0.0050 *M* benzophenone. [j] Only one concentration of quencher, 0.10 *M*, used.

The inefficiency of biphenyl at quenching triplet benzophenone is quite dramatic, naphthalene and the diene being some 145 times more effective. The two *ortho*-substituted biphenyls are even less effective than biphenyl itself. Triphenylene and fluorene display higher energy phosphorescence bands than does biphenyl, and thus might be presumed to possess higher energy triplet states. Nonetheless they are appreciably better quenchers than biphenyl. Actually the quenching behavior of fluorene is somewhat anomalous in that Stern–Volmer plots bend upward. In systems where energy transfer is reversible,[14] self-quenching or quenching by trace impurities could cause this behavior. The value for $k_q\tau$ recorded in Table II was calculated by extrapolating the slopes of the plot in Figure 2 to zero fluorene concentration.

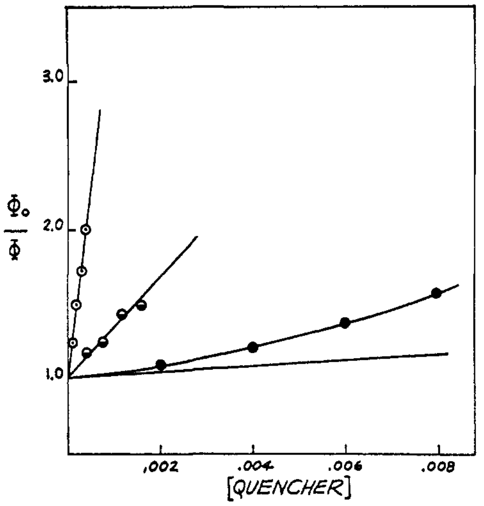

Figure 2. Stern–Volmer plots for quenching of the photoreduction of 0.05 *M* benzophenone: ⊙, naphthalene or 2,5-dimethyl-2,4-hexadiene; ◒, triphenylene; ●, fluorene; lowest line, biphenyl.

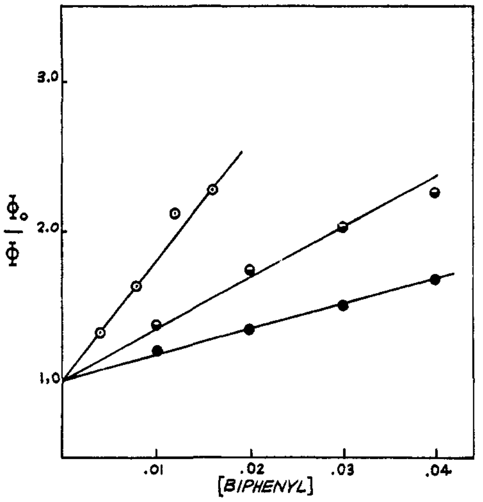

Figure 3. Stern–Volmer plots for quenching of the photoreduction of benzophenone by biphenyl: ⊙, 0.005 *M* benzophenone; ◒, 0.020 *M* benzophenone; ●, 0.050 *M* benzophenone.

Sandros[14] has shown that reversible energy transfer is likely when quenching rate constants are several orders of magnitude below that of diffusion. Consequently a brief study was made of the effect of benzophenone concentration on the quenching efficiency of biphenyl. Two series of samples were prepared and analyzed as above, except that somewhat lower concentrations of biphenyl were used and benzophenone concentrations were 0.020 or 0.0050 *M*. Figure 3,

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(9) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(10) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).

(11) R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

(12) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(13) 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).

(14) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).

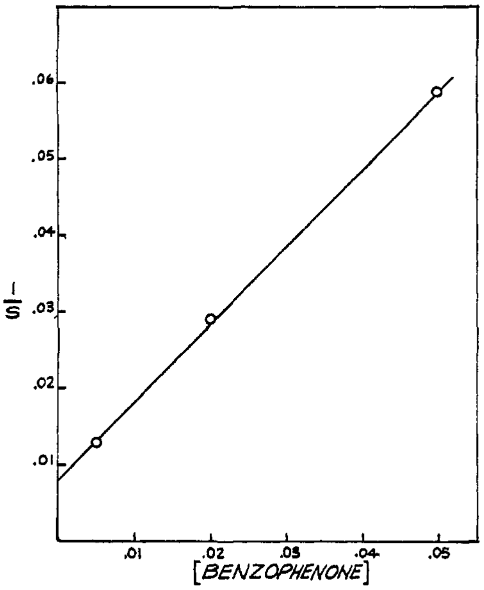

Figure 4. Plot of the reciprocal of the Stern–Volmer slopes in Figure 3 against benzophenone concentration.

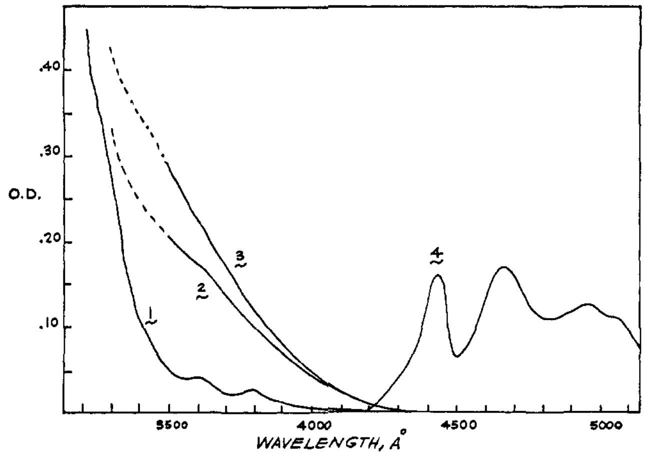

Figure 5. Long-wavelength electronic absorption spectra of biphenyls, all in 5-cm cells: (1) 1.5 *M* biphenyl in benzene *vs.* benzene; (2) 1.0 *M* biphenyl, 6 *M* methyl iodide in 2,2,4-trimethylpentane *vs.* 6 *M* methyl iodide in 2,2,4-trimethylpentane; (3) 0.7 *M* *p*-bromobiphenyl in benzene *vs.* benzene; (4) low-wavelength end of a typical phosphorescence spectrum of biphenyl at 77°K in a glass (ref 21).

which displays Stern–Volmer plots of the results, demonstrates the greater quenching efficiency of biphenyl at lower benzophenone concentrations. The Stern–Volmer slopes are included in Table II.

Straightforward kinetic analysis of reversible energy transfer yields the following modification of the usual Stern–Volmer equation (eq 1). In the system under

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_q\tau[Q]}{1 + \frac{k_{-q}[K]}{k_d'}} \qquad (1)$$

consideration, τ represents the lifetime of triplet benzophenone in the presence of 0.20 *M* benzhydrol and no added quencher; k_q, the rate constant for energy transfer from triplet benzophenone to biphenyl; k_{-q}, the rate constant for energy transfer from triplet biphenyl to ground-state benzophenone; [K], the concentration of benzophenone; [Q], the concentration of biphenyl; and k_d', the rate of decay of triplet biphenyl.

Equation 1 describes the inverse relationship between the slopes of the Stern–Volmer plots and ketone concentration. Letting *S* equal the slope of a given Stern–Volmer plot, the following expression results.

$$\frac{1}{S} = \frac{1}{k_q\tau}\left(1 + \frac{k_{-q}[K]}{k_d'}\right) \qquad (2)$$

Figure 4 depicts the linear adherence of the present results to eq 2. The intercept of 0.0080 yields a value of 125 M^{-1} for $k_q\tau$, and the slope of 0.95 yields a value of 118 M^{-1} for k_{-q}/k_d'.

After corrections for reversibility, the rate of energy transfer from triplet benzophenone to biphenyl turns out to be $^1/_{20}$th the "diffusion-controlled" rate to naphthalene and the diene.

Although no detailed studies were carried out, it is very probable that the *S* values for fluorene and for triphenylene also depend on benzophenone concentration, so that the true values of $k_q\tau$ for them are appreciably greater than those listed in Table II.

$T^* \leftarrow S$ Absorption of Biphenyl. Since the phosphorescence spectrum of biphenyl does not allow correct prediction of its quenching efficiency, a search for the $T^* \leftarrow S$ absorption spectrum of biphenyl was undertaken. A 1.5 *M* benzene solution of biphenyl in a 5-cm cell displays weak, almost featureless absorption beginning around 4200 A, there being two weak but quite distinct maxima at 3790 A ($\epsilon \sim 0.004$) and at 3600 A ($\epsilon \sim 0.006$). Any further structure is masked by intense absorption at wavelengths below 3500 A. This feeble absorption system is assigned to a spin-forbidden $T^* \leftarrow S$ transition for several reasons. Bubbling nitrogen through the cell to remove oxygen decreases the intensity,[15] while inclusion of methyl iodide in the solvent enhances the intensity. Moreover, 4-bromobiphenyl also absorbs more strongly in the same region. No band structure, however weak, could be detected in these presumed heavy atom enhanced[16] $T^* \leftarrow S$ transitions. Typical absorption curves, together with a phosphorescence spectrum from the literature, are presented in Figure 5. Kearns, using the phosphorescence excitation technique, has also found almost featureless $T^* \leftarrow S$ absorption for biphenyl in exactly the same region reported here.[17]

It is apparent that there is little, if any, overlap between emission and absorption and that there is a 10-kcal difference between the highest energy phosphorescence band at 65.5 kcal and the lowest energy absorption band at 75.5 kcal.

Discussion

Spectroscopic Transitions of Biphenyl. The $T^* \leftrightarrow S$ emission and absorption spectra of biphenyl yield estimates of its triplet excitation energy which seem to differ by 10 kcal. This problem of nonoverlapping emission and absorption spectra is not a new one and is a direct result, of course, of the Franck–Condon principle.[18] When the lowest vibrational levels

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(15) (a) D. F. Evans, *Nature*, **176**, 777 (1955); (b) D. Craig, J. Hollas, and G. King, *J. Chem. Phys.*, **29**, 974 (1958).

(16) For a review, see S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(17) A. P. Marchetti and D. R. Kearns, *J. Am. Chem. Soc.*, **89**, 768 (1967).

(18) For an excellent early discussion, see P. Pringsheim, "Fluores-

of ground and excited states possess significantly different equilibrium geometries, true spectroscopic 0–0 transitions are forbidden, and the divergent apparent 0–0 bands observed in emission and absorption spectra represent transitions from one vibrationally relaxed state to a vibrationally excited mode of the other state.

In the present case of biphenyl, it would appear that there exists a gross geometric difference between the ground state and the excited triplet state. The highest energy band in the phosphorescence spectrum at 65.5 kcal probably should be reinterpreted as a transition from the triplet state in its equilibrium geometry to a vibrationally or rotationally excited ground state. Likewise the $T^* \leftarrow S$ absorption band at 75.5 kcal probably represents a transition from vibrationally and rotationally relaxed ground state to a nonequilibrium conformation of the excited triplet. The true 0–0 energy difference must lie somewhere intermediate between 65.5 and 75.5 kcal and represents a *nonspectroscopic* transition which is forbidden in radiative processes but allowed in bimolecular energy-transfer reactions. The long tail out to 4200 A in the $T^* \leftarrow S$ absorption spectrum probably can be attributed to absorption by the small percentages of ground-state molecules in nonequilibrium geometries, as will be discussed later.

This exact an interpretation would not be justified by the spectroscopic data alone, but it is the only one consistent with the quenching results now to be discussed.

Triplet-Energy Transfer Involving Biphenyl. The data in Tables I and II for naphthalene, the stilbenes, and the dienes provide further evidence that the efficiency of triplet-energy transfer in solution is equally great to all compounds whose triplet energies are sufficiently lower than that of the donor. Biphenyl clearly is not such a "diffusion controlled" quencher toward the three ketones studied. The marked inefficiency with which biphenyl quenches triplet benzophenone indicates that the triplet energy of biphenyl is at least as great as that of the ketone.

Rate constants for triplet-energy transfer from the various ketones to biphenyl can be estimated. Flash spectroscopic studies[3,5] have indicated that naphthalene, the stilbenes, and conjugated dienes all quench triplets with excitation energies as high as those of the ketones with what seems to be a maximum bimolecular quenching rate constant of $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in benzene. The rate constant for quenching of triplet butyrophenone ($E_T \sim 72.5$ kcal[19]) by biphenyl is thus calculated to be $2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, while that for the quenching of triplet benzophenone ($E_T = 69.5$ kcal)[19] by biphenyl is only $2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. Quenching rate constants have not been measured in isopropyl alcohol; however, the rate constant for diffusion can be calculated from the viscosity[20] as $4.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. If it is assumed that naphthalene quenches triplet propiophenone ($E_T = 76.4$ kcal[12]) with this rate constant, that for biphenyl would be $3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. This value is somewhat higher than that estimated for the lower energy butyrophenone, but it is noteworthy that the efficiency of triplet-energy transfer to biphenyl is measurably less than maximal even in a fairly viscous solvent and with a quite high-energy donor.

The inefficiency in the quenching of triplet butyrophenone by biphenyl is reasonably readily explained. In order for vertical-energy transfer to take place, in which process the geometry of the biphenyl remains constant, a donor with at least a 75.5-kcal triplet energy is required. However, as will be discussed below, the vibrationally relaxed triplet of biphenyl, of a geometry substantially different from that of the ground state, lies no more than 70 kcal above the ground state. Consequently, energy transfer to biphenyl involves *nonvertical* transitions in which the geometry of the biphenyl changes appreciably. The steric requirements for such an energy-transfer process are undoubtedly greater than for vertical-energy transfers, and the observed difference in the rates with which biphenyl and the "diffusion-controlled" quenchers quench triplet butyrophenone is some measure of this steric effect. An identical explanation has been advanced by Hammond and his co-workers for the behavior of the stilbenes.[5,13]

It was hoped that the triplet energy of propiophenone was sufficiently large that vertical-energy transfer to biphenyl would be possible. Whatever the reason, energy transfer seems to be not much more efficient than from the lower energy triplet butyrophenone.

The quenching results with benzophenone are the most informative. A quenching rate constant of $2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ suggests that energy transfer may be slightly endothermic.[14] The first problem, then, in determining the true triplet energy of biphenyl involves ascertaining the true triplet energy of benzophenone. Hammond and co-workers[12] have reported that the 0–0 band in the phosphorescence spectrum of benzophenone in hydrocarbon solvents occurs at 68.5 kcal. Kearns and Case, however, have noted a 2-kcal separation between phosphorescence and absorption 0–0 bands.[19] Consequently, the true triplet excitation energy of benzophenone in benzene probably is approximately 69.5 kcal. As pointed out above, with butyrophenone as donor, the rate constant for energy transfer does not seem to exceed $2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. The further decrease by a factor of 8 upon going to triplet benzophenone donor could be compounded of further steric restrictions plus new energetic requirements. Unfortunately, there is no way of guessing the contribution of steric effects alone in depressing the rate of nonvertical-energy transfer when biphenyl must be twisted all the way to its equilibrium triplet geometry. If the further steric effect were minor, the eightfold total rate decrease would imply that energy transfer was approximately 1 kcal endothermic. If, however, severe steric requirements are the major contributor to the total rate decrease, energy transfer could be thermoneutral or even slightly exothermic. Therefore 69.5 ± 1.0 kcal is perhaps the best estimate that can be made for the true 0–0 energy for the $T^* \leftrightarrow S_0$ transition of biphenyl. Such a value is in good agreement with the suggested interpretation of the spectroscopic data, being somewhat less than midway between the two divergent 0–0 bands.

Since these experiments provide no knowledge of the lifetime of triplet biphenyl, a discussion of the value of

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cence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, pp 299–303.

(19) D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966).

(20) A. D. Osborne and G. Porter, *Proc. Roy. Soc.* (London), **A284**, 9 (1965).

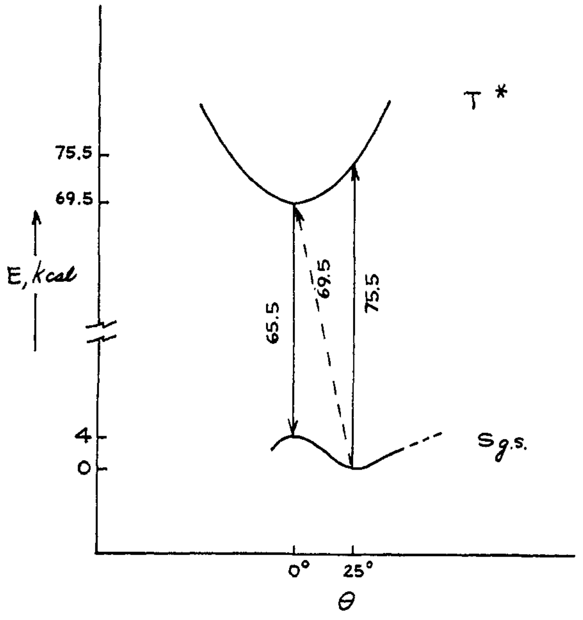

Figure 6. Spectroscopic (solid lines) and nonspectroscopic (dashed line) T* ↔ S transitions in biphenyl. Curves represent supposed potentials for the two states as a function of dihedral angle θ between the rings.

k_{-q}/k_d' obtained from the slope of Figure 4 would not be profitable. As soon as flash spectroscopic studies allow determination of the value of k_d', a comparison of k_q and k_{-q} values ought to provide an even better estimate of the triplet energy of biphenyl.

The Triplet State of Biphenyl. The spectroscopic data and the quenching results considered together indicate that the geometry of biphenyl in its triplet state must differ considerably from that of its ground state. The most stable conformation of ground-state biphenyl depends strongly on the medium. The dihedral angle between the two rings is 40–45° in the gas phase,[21] 20–25° in solution,[22] and 0° in the crystalline state.[23] Consequently, the triplet state in solution must deviate considerably from a 20–25° twist, and a large body of evidence points to a perfectly planar conformation.

ortho substituents are well known to increase the dihedral angle in biphenyls and consequently would be expected to make for better quenching if the triplet state were more twisted than the ground state and worse quenching if the triplet state tended toward planarity. The latter effect is observed. In 1944 Lewis and Kasha reported that *ortho* substituents shift the phosphorescence spectrum of biphenyl to higher energies,[24] presumably because of steric crowding in planar excited states.

Hirota has provided seemingly incontrovertible evidence regarding the geometry of triplet biphenyl. He measured the T* ← S absorption spectra of a few compounds by a modified phosphorescence excitation method, in which *crystals* of the subject compound were doped with a compound of lower triplet energy to trap the excitation.[25] The T* ← S spectrum of biphenyl so obtained displays a 0–0 band at 65.5 kcal in exact agreement with the highest energy phosphorescence band. Consequently the 65.5-kcal transition in biphenyl must take place between planar conformations of both ground and triplet states. Such a transition is a true 0–0 transition in the crystal, but not in solution where the most stable conformation of the ground state is twisted.

Figure 6 depicts a schematic energy diagram for the various T ↔ S transitions of biphenyl in solution, the curves representing potentials for twisting around the C–C bond connecting the two rings. The two vertical solid arrows represent spectroscopic transitions between states of identical geometry, while the slanted dotted line represents the nonspectroscopic transition which can take place in the relatively slow nonvertical energy-transfer process. The potential for twisting triplet biphenyl is steeper than that for the ground state in accord both with theoretical expectations and with the experimental observation that the 0–0 energy is somewhat less than midway between the highest energy phosphorescence band and the lowest energy absorption band.

The combination of spectroscopic and quenching results indicate that the ground-state conformation which possesses the equilibrium geometry of the triplet state is about 4 kcal excited relative to the favored ground-state conformation. Theoretical estimates predict a very shallow potential for twisting the rings in biphenyl,[26,27] and 5 kcal is the largest estimate[27] yet made for the difference between twisted and planar ground-state biphenyl. Of course the impossibility of resolving optical isomers of 2,2′-disubstituted biphenyls unless the *ortho* substituents are extremely bulky is strong experimental evidence for the low activation energy required to twist the rings of biphenyl.

Choosing the maximum at 3790 A in the T* ← S absorption spectrum of biphenyl as the "lowest energy spectroscopic transition" instead of some point on the long tail out to 4200 A may have seemed somewhat arbitrary, and in a sense was. With the shallow potential for twisting the rings, a fairly large percentage of ground-state molecules must exist with twists between 0 and 25°, and for that matter greater than 25°. For example, if a planar molecule is excited 4 kcal and one twisted 10° only 2 kcal, simple Boltzmann statistics predict that 0.2 and 4% of the ground state molecules will be planar and twisted 10°, respectively, at room temperature. Figure 6 illustrates that T* ← S absorption by biphenyl molecules twisted less than the favored 20–25° occurs at *longer* wavelengths than absorption by the majority of molecules which are in the favored ground-state conformation. The long tail, then, most likely is composed of spectroscopic transitions by small percentages of ground-state molecules in nonequilibrium conformations, and is not particularly unusual except in its 400-A length. The band at 3790 A is not, then, the lowest energy T* ← S spectroscopic transition occuring in biphenyl, but it is the lowest energy spectroscopic transition from the lowest vibrational–rotational level of the ground state. It is important to note that the suggested interpretation of combined quenching and phosphorescence data implies that it would be incorrect to call some point near 69.5

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(21) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949).

(22) H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340 (1959).

(23) J. Trotter, *Acta Cryst.*, **14**, 1135 (1961).

(24) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(25) N. Hirota, *J. Chem. Phys.*, **44**, 2199 (1966).

(26) F. Adrian, *ibid.*, **28**, 608 (1958).

(27) I. Fischer-Hjalmars, *Tetrahedron*, **19**, 1805 (1963).

kcal in the absorption spectrum the 0–0 transition. Absorption at this energy represents a transition between two states both of which are weakly torsionally excited.

Since the triplet state of biphenyl seems to be planar, photosensitized racemization of optically active biaryls ought to occur with ease. Mislow has already reported the direct photoracemization of several biaryls.[28] In this regard, the effects of substituents on the quenching efficiency of biphenyl promise to be very interesting, since k_q, k_{-q}, and k_d' all ought to vary considerably, and a study of such effects is in progress.

The fact that the triplet energy of biphenyl is higher than can be estimated from its phosphorescence spectrum helps clarify some photochemistry. Zimmerman has reported that biphenyl is only $^{1}/_{80}$th as effective as naphthalene at quenching the photorearrangement of a cyclic unsaturated ketone.[29] He measured the triplet energy of the ketone as 71 kcal, but found it difficult to reconcile this value with a 65.5-kcal triplet energy for biphenyl. The matter is of some importance because of the considerable speculation and controversy regarding the nature of the reacting triplets of enones. The higher value for the triplet energy of biphenyl is much more consistent with a ketone triplet of 71-kcal excitation energy.

Experimental Section

Solvents. Reagent grade benzene was washed with sulfuric acid, dried, and distilled from phosphorus pentoxide. Reagent grade isopropyl alcohol was distilled from sodium.

Chemicals. Propiophenone (Eastman) and butyrophenone (Aldrich) were distilled under reduced pressure and then recrystallized several times from pentane. Eastman White Label benzophenone was recrystallized from ligroin. Columbia Organics tetradecane required extensive washings with sulfuric acid before drying and distillation under reduced pressure. Matheson Coleman and Bell benzhydrol was used without further purification. Naphthalene, biphenyl, fluorene, *trans*-stilbene, 2-fluorobiphenyl (Columbia Organics), and 2-chlorobiphenyl (K & K Laboratories) were all recrystallized once from ethanol. Aldrich triphenylene was recrystallized several times until white. The melting points of all the solid quenchers checked with those reported in the literature. Aldrich *cis*-stilbene was distilled under reduced pressure. Aldrich piperylene was distilled and analyzed by glpc analysis as 98% *cis*-and *trans*-piperylene and 2% cyclopentene. Aldrich 2,5-dimethyl-2,4-hexadiene was recrystallized from itself.

Absorption Spectra. A Cary 14 spectrophotometer was employed and solutions were contained in 5-cm cells Concentrations and results are presented in Figure 5.

Preparation of Samples. For the propiophenone system, one stock solution 0.50 *M* in propiophenone was prepared by weighing the appropriate amount of ketone in a 25-ml volumetric flask and filling to volume with isopropyl alcohol. Stock solutions 0.020 *M* in naphthalene and 0.029 *M* in biphenyl were prepared similarly. A 2-ml portion of the ketone solution was pipetted into each of nine 10-ml volumetric flasks, one of which was immediately filled to volume with solvent. From 1 to 4 ml of each of the quencher solutions was pipetted into each of the other flasks before they were filled to volume. Then 2.6 ml of each solution was placed in separate Exax tubes with a syringe. The tubes were standard 13 × 100 culture tubes which had been washed and dried before being constricted about 1 in. from the top to allow sealing. The tubes with the samples in them were attached to a vacuum line and put through three freeze–pump–thaw cycles before being sealed *in vacuo* at 0.002 mm.

Samples were prepared quite similarly for the benzophenone and butyrophenone systems except that benzene was used as solvent and the ketone stock solutions were 0.250, 0.100, or 0.0250 *M* in benzophenone and 1.00 *M* in benzhydrol in the first case and 1.00 *M* in butyrophenone and 0.02–0.03 *M* in tetradecane in the latter.

Irradiation of Samples. In any given run degassed tubes containing four different concentrations of each of several quenchers were irradiated in parallel with two or three samples containing only ketone, all for the same length of time. Irradiations were performed in a "merry-go-ground" apparatus,[30] consisting essentially of a rotating turntable with the light source and filters at the center and windows of identical area allowing radiation to enter the various sample compartments. This design ensured that the same intensity radiation impinged upon each sample. Since each sample contained the same concentration of ketone, the amount of irradiation absorbed by each sample was identical; since each tube contained the same volume of liquid, the relative amount of reaction in each tube was directly proportional to the quantum yield. Corning No. 7-83 filter combinations were used to isolate the 3660-A line of a Hanovia 450-w medium-pressure mercury lamp, and a 1-cm path of 0.002 *M* potassium chromate in 5% aqueous potassium carbonate was used to isolate the 3025–3130-A lines. The entire apparatus was immersed in a water bath, and the temperature during irradiation was maintained at 25 ± 1°.

Analyses of Samples. The disappearance of propiophenone and benzophenone was measured on a Gilford Model 200 spectrophotometer. Samples with no quencher were carried to approximately 50% conversion. Analyses were made at 3400, 3500, 3600, and 3700 A for benzophenone and 3400, 3450, and 3500 A for propiophenone. Measured per cent reactions varied by less than 1% at the various wavelengths. The propiophenone and dilute benzophenone samples were analyzed in 10-mm cells, the 0.050 *M* benzophenone samples in 1-mm cells. The dilute ketones did not absorb all the light incident upon them, and corrections for this were made in calculating relative quantum yields.

The photoelimination of butyrophenone was monitored by measuring the yields of acetophenone formed by glpc analysis. All analyses were performed on an Aerograph Model 600-D Hy-Fi with a 6 ft × $^{1}/_{8}$ in. column containing 4% QF-1 and 1% Carbowax 20M on 60–80 mesh Chromosorb P, with a column temperature of 105–110° and a nitrogen flow of 30 ml/min. A Leeds and Northrup Model H recorder fitted with a disk integrator allowed the area ratios of acetophenone to tetradecane to be measured with 1% reproducibility. Area ratio were converted to mole ratios by calibrating the column with known mixtures.

Acknowledgment. Grants from the National Science Foundation and the Office of Naval Research are gratefully acknowledged. A grant from Research Corporation allowed preliminary work to be begun and is particularly appreciated. Professor Kearns very generously provided preprints of his work.

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[28] K. Mislow and A. J. Gordon, *J. Am. Chem. Soc.*, **85**, 3521 (1963).

[29] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 159, 1965 (1966).

[30] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).