Intramolecular Triplet Energy Transfer in Flexible Molecules: Electronic, Dynamic, and Structural Aspects

Peter J. Wagner* and Petr Klán[†]

Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48824

Abstract: Exothermic intramolecular triplet energy transfer (TET) rate constants in various flexible bichromophoric systems D-$(CH_2)_n$-O-A (D = benzoyl, 4-methylbenzoyl; A = 2-naphthyl, 4-, 3-, 2-biphenyl; n = 3−14) have been determined from steady-state quenching and quantum yield measurements. The magnitude of the rate constants in molecules where n = 3 is comparable to those in molecules with a rigid spacer between chromophores, so that a through-bond mechanism is presumed to remain important. A very gradual drop in TET rate constants as the connecting polymethylene chain becomes longer indicates that through-space interactions compete and apparently provide the only mechanism responsible for transfer when $n \geq 5$. Rate constants in long molecules (n = 11−14) remain remarkably high ($\sim 10^8$ s^{-1})—lower than in those with four-atom tethers by only 1 order of magnitude. This effect is explained on the basis of rapid conformational equilibria always keeping a sufficient fraction of the molecules coiled so that the two chromophores are close enough to interact within 10 ns, the time required for the competing γ-hydrogen abstraction used to monitor triplet lifetimes. Energy transfer accounts for 40−75% of triplet decay for the longer molecules. This high efficiency indicates that only a small fraction involves static quenching in ground-state conformers with the two ends within 4 Å. The majority must represent a combination of rate-determining bond rotations to such geometries and equilibrated conformations with their ends farther apart but still able to undergo energy transfer within 10 ns. Thus, the measured rate constants are, in fact, a weighted average of three different conformational mechanisms. The decrease in rate constant with tether length is not monotonic: a relative increase in rate for medium-chain-length molecules is explained by a larger number of favorable conformers and further, in biphenyl derivatives, by a rotation along the terminal O−C bond between the tether and the aromatic ring. As was expected, replacement of the polymethylene tether with poly(ethylene oxide) promotes better flexibility and thus higher transfer rates. Rate constants were found to be lower by a factor of ~ 2 when biphenyl rather than naphthyl is the acceptor, in agreement with earlier bimolecular measurements. With the 4-methylbenzoyl group (π,π^* lowest triplet) as donor instead of benzoyl (n,π^* lowest triplet), a small ($\sim 1.5\times$) but consistent rate increase occurred for all tether lengths.

Introduction

Photosensitization induced by electronic energy transfer is an important process in nature and thus has been one of the most studied aspects of photochemistry. It is generally accepted that energy transfer from an excited triplet to the ground state of another chromophore proceeds via an exchange mechanism, in which the rate constant shows an inverse exponential dependence on the distance between the two chromophores.[1,2] It is also important that the chromophores have the proper electronic orientation.[3,4] For a solution encounter between excited donor and acceptor molecules, the actual energy transfer rate usually exceeds 10^{10} s^{-1} when energy transfer is exothermic,[5] such that bimolecular energy transfer is partially or fully diffusion controlled, depending on solvent viscosity.[6,7] When

the donor and the acceptor are in a single molecule, the same factors presumably hold, with the added complexity that the intervening molecular skeleton affects the distance between the two chromophores.

There has been a long-standing interest in determining the extent to which intramolecular electronic interactions between two functional groups occur by a through-bond or a through-space mechanism. Following studies with Miller that revealed a strong through-bond component in intramolecular electron transfer, Closs and co-workers extended this interest to triplet energy transfer (TET).[8] They investigated compounds in which a 2-naphthyl group was connected via a rigid spacer to a 4-benzoylphenyl chromophore, with the spacer either a cyclohexane or a decalin ring.[9] Rate constants for such transfer dropped ~ 1 order of magnitude for each additional bond between chromophores. When the chromophores were attached

†Katedra organickè chemie, Masarykova univerzita, Kotl·⁻sk• 2, 611 37 Brno, Czech Republic.

(1) (a) Dexter, D. L. *J. Chem. Phys*. **1953**, *21*, 836. (b) Yardley, J. T. *Introduction to Molecular Energy Transfer*; Academic Press: New York, 1980.

(2) Lamola, A. A. Electronic Energy Transfer in Solution: Theory and Applications. In *Techniques of Organic Chemistry*; Weisberger, A., Ed.; Wiley: New York, 1969; Vol. 14.

(3) Letchen, P.; Turro, N. J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 314.

(4) Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc*. **1985**, *107*, 5806.

(5) Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500.

(6) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc*. **1968**, *90*, 2232.

(7) Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799. Makemura, T.; Baba, H.; Fujita, M. *Bull. Chem. Soc. Jpn*. **1973**, *46*, 2625.
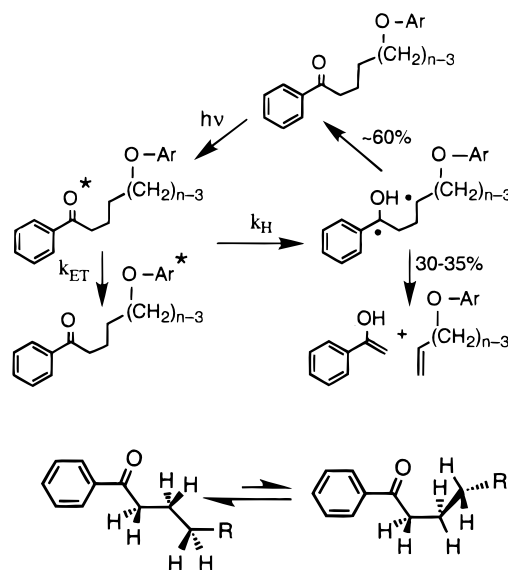
(8) (a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc*. **1983**, *105*, 670. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (c) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173.

to the spacer in all-equatorial positions, TET rate constants were about 1 order of magnitude higher than those for equatorial−axial attachments, consistent with a predominant through-bond mechanism. It is interesting that these studies extrapolate to the low rate constant measured in a very early study with a steroid spacer and the same chromophores.[10]

Studies of chemical reactions or physical processes occurring between groups attached at the ends of a flexible tether are widespread in the literature.[11] However, intramolecular triplet energy transfer in flexible molecules has been studied only for systems with relatively short tethers. Some early phosphorescence measurements[12] established only that TET is very rapid. Cowan and Baum observed a continuous drop in rate constants of energy transfer as the number of methylenes connecting benzoyl and styryl chromophores increased from two to four.[13] In α-benzoyl-ω-azidoalkanes, quenching of the benzoyl chromophore's triplet chemistry by the azido group decreased 3 orders of magnitude as the tether length increased from three to five methylenes.[14] Since these effects were comparable to those observed in Closs's more rigid systems, it was impossible to distinguish between through-space and through-bond effects. To distinguish these, we investigated energy transfer in the cinnamyl esters of ω-benzoylcarboxylic acids.[15] For these flexible 4−7-atom tethers, energy transfer rate constants decreased much more slowly than in Closs's rigid systems, and we concluded that through-space transfer became the predominant mechanism in molecules with longer chains. We made a similar conclusion in a study of energy transfer in unsymmetric diketones.[16]

With these two examples in hand, we decided to extend our studies to even longer α,ω-substituted polymethylenes with chromophores as similar as possible to those used by Closs. In a preliminary communication, we reported our study of intramolecular TET in ω-naphthyl- and ω-4-biphenylylalkanophenones, in which the donor is the benzoyl group.[17] Although phenyl alkyl ketones have slightly higher triplet energies than benzophenone, their triplets are very similar electronically, and Closs has shown that acetophenone and benzophenone donors provide nearly identical TET rate constants to naphthalene acceptor.[18] We found that transfer rate constants decrease only 1 order of magnitude as the tether length increases from 5 to 14 methylenes and concluded, as we had in our 1992 papers, that energy transfer occurs primarily by through-space interactions in these long, flexible molecules. We have expanded this work to include additional donors and acceptors, and we now wish to report our complete findings on how electronic, dynamic, and structural factors can change the course of intramolecular TET.

(9) (a) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652. (b) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.

(10) Keller, R. A.; Dolby, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 1293. Breen, D. E.; Keller, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 1935.

(11) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491.

(12) Lamola, A. A.; Leemakers, P. A.; Byers, G. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 2322.

(13) Cowan, D. O.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 1153.

(14) Wagner, P. J.; Scheve, B. J. *J. Am. Chem. Soc.* **1979**, *101*, 378.

(15) Wagner, P. J.; El-Taliawi, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 8325.

(16) Wagner, P. J.; Giri, B. P.; Frerking, H. W., Jr.; DeFrancesco, J. *J. Am. Chem. Soc.* **1992**, *114*, 8326.

(17) Klan, P.; Wagner, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 2198.

(18) Sigman, M. E.; Closs, G. L. *J. Phys. Chem.* **1991**, *95*, 5012.

Scheme 1

Strategy

The Norrish type II reaction[19] has proven to be a uniquely useful tool for monitoring competing triplet reactions, both inter- and intramolecular. This reaction proceeds exclusively via intramolecular γ-hydrogen abstraction by the excited carbonyl group, which produces a 1,4-biradical as the primary photoproduct.[20] In simple phenyl and substituted phenyl ketones, the intersystem crossing quantum yield is unity,[21] and hydrogen abstraction proceeds exclusively from the triplet excited state.[20] The biradical undergoes three competing reactions: cleavage to an alkene and the enol of acetophenone, which rapidly tautomerizes to acetophenone; ∼10% cyclization to a 1-aryl-cyclobutanol; and disproportionation back to ground-state ketone. The latter reaction can be suppressed by use of Lewis base additives.[20,22] When the molecule contains another functional group with which the triplet carbonyl can react, both the quantum yield for type II product formation and the triplet lifetime are reduced proportionally, providing two separate measures of the relative rates for hydrogen abstraction and the competing reaction. Since energy transfer is one such reaction that can compete with hydrogen abstraction, we utilized this approach in our earlier energy transfer studies[14−16] and have applied it in this work as well, the kinetics of γ-hydrogen abstraction being adopted as the "system clock" to calculate energy transfer rate constants. Scheme 1 exemplifies the competition between energy transfer and the Norrish type II reaction, Ar being any of the aromatic groups that we studied. Since hydrogen abstraction is unavoidable with a polymethylene spacer between donor and acceptor, quantum yield studies are absolutely required in order to assess the ratio of energy transfer and hydrogen abstraction. Picosecond flash kinetics would be required in order to measure triplet lifetimes directly, but quenching studies have been shown to be just as accurate. These have shown that the rate constants for γ-hydrogen abstraction
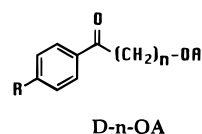
(19) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. Wagner, P. J.; Park, B.-S. Photoinduced Hydrogen Atom Abstraction by Carbonyl Compounds. In *Organic Photochemistry*; Padwa, A., Ed.; 1991; Vol. 11, p 111.

(20) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898. Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.

(21) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

(22) Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.

Scheme 2

D-n-OA

D = Bz (R = H); MeBz (R = CH$_3$)

A = Ph (phenyl); Np (2-naphthyl);

2, 3, 4Bp (2/3/4-biphenylyl)

Table 1. Photokinetics of ω-Phenoxy Ketones in Cyclohexane[a]

D-n-OA	Φ_{II}	$k_q\tau$, M^{-1}	$1/\tau$ (k_H), 10^8 s^{-1}
Bz-3-OPh	0.45 ± 0.00	31 ± 0.4	2.6
Bz-4-OPh	0.44 ± 0.01	232 ± 16	0.34
Bz-5-OPh	0.35 ± 0.01	90 ± 0.3	0.89
Bz-7-OPh	0.29 ± 0.00	62 ± 2.3	1.3
Bz-10-OPh	0.26 ± 0.01	57 ± 1.2	1.4
Bz-11-OPh	0.26 ± 0.01	58 ± 0.4	1.4
MeBz-3-OPh	0.61 ± 0.02	153 ± 2.7	0.50
MeBz-4-OPh	0.56 ± 0.02	1090 ± 87	0.07
MeBz-5-OPh	0.43 ± 0.02	412 ± 1.5	0.19
Bz-3-O-2-OPh	0.44 ± 0.01	25 ± 1.6	3.2

[a] Measured at room temperature; values represent average of two measurements.

Table 2. Photokinetics of Naphthyloxy Bichromophores in Cyclohexane[a]

D-n-OA	Φ_{II}	$k_q\tau$, M^{-1}	$1/\tau$, 10^8 s^{-1}	k_H, 10^8 s^{-1} from Φ
Bz-3-ONp	0.13 ± 0.00	4.2 ± 0.1	19.0	5.5
Bz-4-ONp	0.04 ± 0.00	16.3 ± 0.5	4.9	0.4
Bz-5-ONp	0.16 ± 0.00	19.5 ± 0.1	4.1	1.9
Bz-6-ONp	0.16 ± 0.00	22.2 ± 0.7	3.6	1.8
Bz-7-ONp	0.17 ± 0.00	23.2 ± 0.0	3.4	2.0
Bz-9-ONp	0.11 ± 0.02	15.0 ± 1.4	5.3	2.1
Bz-10-ONp	0.13 ± 0.01	13.6 ± 1.1	5.9	2.9
Bz-11-ONp	0.18 ± 0.00	24.7 ± 0.2	3.2	2.2
Bz-14-ONp	0.15 ± 0.00	30.8 ± 3.0	2.6	1.5
MeBz-3-ONp	0.03 ± 0.00	3.4 ± 0.0	23.5	1.2
MeBz-4-ONp	0.01 ± 0.00	15.7 ± 0.2	5.1	0.1
MeBz-5-ONp	0.03 ± 0.00	20.3 ± 0.0	3.9	0.3
MeBz-6-ONp	0.04 ± 0.00	23.7 ± 0.6	3.4	0.35
MeBz-7-ONp	0.05 ± 0.00	25.8 ± 1.1	3.1	0.4
MeBz-11-ONp	0.06 ± 0.00	28.8 ± 1.6	2.8	0.5

[a] Measured at room temperature; values represent average of two measurements.

do not vary significantly as the alkyl group gets longer.[23,24] Such rate constants depend on the equilibrium population of gauche conformers around the $\alpha-\beta$ C–C bond, in which a γ-hydrogen is within bonding distance of the carbonyl. Scheme 1 also shows this equilibrium. We have performed some simple molecular mechanics and semiempirical calculations that indicate no significant difference in the equilibrium as R gets larger.

Based on the following known triplet excitation energies, energy transfer in all systems except the ω-phenoxyketones must be exothermic and irreversible (all values in kcal/mol): benzoyl, $\sim$73;[25] 4-methylbenzoyl, $\sim$72;[25,26] phenoxy, $\sim$81;[27] 2-naphthyloxy, $\sim$62;[28] 2-, 3-, and 4-biphenyloxy, 68–69.[29]

Results

Scheme 2 lists the bichromophoric ketones we have studied. They were prepared by standard synthetic methods and purified to 99+% in all cases, except for compounds with the 3-biphenyl group as acceptor, which contained 2–3% of their 4-biphenyl isomers. The ω-phenoxy compounds were prepared as model compounds in which there could be no internal energy transfer, since the triplet energy of anisole is much higher than that of phenyl ketones.[27] The 7-phenoxy and -(4-biphenyl)oxy versions of 1-phenyl-5-oxa-1-heptanone (Bz-3-O-2-OA) were also prepared and studied.

Cyclohexane or benzene solutions 0.001 M in bichromophore and containing different concentrations of 2,5-dimethyl-2,4-hexadiene as quencher were irradiated at 366 nm, where only the benzoyl group absorbs. Either valerophenone or 4-methylvalerophenone solutions, also 0.001 M, were irradiated simultaneously as actinometers for quantum yield measurements.[22,26] Triplet lifetimes were determined by Stern–Volmer steady-state quenching techniques.[32] All Stern–Volmer plots were linear, with correlation coefficients 0.97–0.99, their slopes equaling $k_q\tau$. The type II product yields (acetophenone or 4-methylacetophenone) were determined by HPLC; conversions

(23) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.

(24) Pitts, J. N., Jr.; Burley, D. R.; Mani, J. C.; Broadbent, A. D. *J. Am. Chem. Soc.* **1968**, *90*, 5900.

(25) Kearns, D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087. Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466.

(26) Wagner, P. J.; Thomas M. J.; Harris, E. *J. Am. Chem. Soc.* **1976**, *98*, 7675.

(27) *Handbook of Photochemistry*; Murov, S. L., Carmichael, I., Hug, G. L., Eds.; Marcel Dekker: New York, 1993.

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

(29) Estimated from E_T = 64 kcal/mol for 4-hydroxybiphenyl[30] and the large Stokes shift for biphenyls.[31]

(30) Taylor, H. V.; Allred, A. L.; Hoffman, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 3215.

(31) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820. Hutchison, C. A., Jr.; Kemple, M. D. *J. Chem. Phys.* **1979**, *71*, 866. Takei, Y.; Yamaguchi, T.; Osamura, Y.; Fuke, K.; Kaya, K. *J. Phys. Chem.* **1988**, *92*, 577.

(32) Stern, O.; Volmer, M. *Phys. Z.* **1919**, *20*, 183. Wagner, P. J. *Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989; Vol. 2, p 38.

were kept under 15%. Minor HPLC peaks were observed in some ketones and assumed to be the expected cyclobutanol coproducts.

Tables 1–3 list Norrish type II quantum yield, $k_q\tau$, and $1/\tau$ values for all systems. Quantum yields were corrected for optical density at 366 nm in cyclohexane or benzene. Most bichromophores used in this work were not very soluble in cyclohexane, and therefore it was difficult to obtain precise optical density and molar absorbtivity values in this solvent. For many of the longer molecules, 0.001 M concentration was nearly a saturated solution. Typical values of molar absorbtivities ϵ_{366} were as low as 3–5 L mol^{-1} cm^{-1}. Reciprocal lifetimes $1/\tau$ were calculated from $k_q\tau$ and the known bimolecular rate constants (k_q), 8×10^9 M^{-1} s^{-1} for cyclohexane[6] and 6×10^9 M^{-1} s^{-1} for benzene.[4] It is possible that increasing the length of the bichromophore could lower the probability of energy transfer during a solution encounter and thus cause k_q to drop slightly, but the effect would be masked by the near diffusion control. Therefore, it was assumed throughout that the near-diffusion-controlled values of k_q measured for various smaller ketones[4] remain constant as n increases.

Energy Transfer Rate Constants. Energy transfer rate constants (k_{ET}) were calculated from the measured triplet lifetimes by two methods: (1) subtracting $1/\tau$ of the model ω-phenoxy compound from that of the corresponding bichromophore and (2) partitioning triplet lifetimes between hydrogen abstraction and energy transfer by comparing quantum yields to those of the model compounds. The k_{ET} values are listed in Tables 4 and 5, along with quantum yields for energy transfer as gleaned from the measured decreases in triplet lifetimes and acetophenone quantum yields. Determination of γ-hydrogen

Table 3. Photokinetics of Biphenyloxy Bichromophores in Cyclohexane[a]

D-n-OA	Φ_{II}	$k_q\tau$, M^{-1}	$1/\tau$, 10^8 s^{-1}	k_H, 10^8 s^{-1} from Φ
Bz-3-O4Bp	0.17 ± 0.02	7.7 ± 0.6	10.4	3.9
Bz-4-O4Bp	0.05 ± 0.00	20.7 ± 0.3	3.9	0.45
Bz-5-O4Bp	0.13 ± 0.00	27.3 ± 0.9	2.9	1.1
Bz-6-O4Bp	0.14 ± 0.00	30.4 ± 0.2	2.6	1.1
Bz-7-O4Bp	0.17 ± 0.01	32.5 ± 0.1	2.5	1.5
Bz-9-O4Bp	0.13 ± 0.00	20.5 ± 0.2	3.9	1.8
Bz-10-O4Bp	0.17 ± 0.01	23.3 ± 0.4	3.4	2.1
Bz-11-O4Bp	0.21 ± 0.01	33.4 ± 0.7	2.4	1.9
Bz-14-O4Bp[b]	0.24 ± 0.00	28.4 ± 0.2	2.1	1.9
Bz-3-O3Bp	0.20 ± 0.01	10.1 ± 0.1	7.9	3.5
Bz-6-O3Bp	0.17 ± 0.01	32.8 ± 0.2	2.4	1.3
Bz-7-O3Bp	0.18 ± 0.01	27.5 ± 0.0	2.9	1.8
Bz-9-O3Bp[c]	0.15	36	2.2	1.2
Bz-10-O3Bp	0.18 ± 0.01	28.6 ± 0.1	2.8	1.9
Bz-14-O3Bp	0.17 ± 0.00	35.7 ± 0.5	2.2	1.4
Bz-3-O2Bp	0.23 ± 0.01	11.9 ± 0.1	6.7	3.4
Bz-4-O2Bp	0.05 ± 0.00	36.7 ± 0.0	2.2	0.2
Bz-5-O2Bp	0.17 ± 0.00	32.5 ± 0.3	2.5	1.2
Bz-6-O2Bp	0.13 ± 0.00	25.7 ± 0.6	3.1	1.3
Bz-7-O2Bp	0.13 ± 0.00	21.6 ± 0.4	3.7	1.7
Bz-9-O2Bp	0.13 ± 0.01	29.8 ± 0.6	2.7	1.3
Bz-10-O2Bp	0.13 ± 0.00	23.9 ± 0.9	3.3	1.65
Bz-11-O2Bp	0.19 ± 0.01	35.7 ± 2.0	2.2	1.6
Bz-14-O2Bp	0.20 ± 0.01	39.2 ± 0.6	2.0	1.5
MeBz-3-O4Bp	0.04 ± 0.00	8.9 ± 0.1	9.0	0.6
Bz-3-O-2-O4Bp	0.17 ± 0.00	10.5 ± 0.9	7.6	2.9

[a] Measured at room temperature; values represent average of two measurements. [b] In benzene. [c] Single measurement.

Table 4. Intramolecular Energy Transfer Rate Constants in Naphthyloxy Ketones

D-n-OA	k_{ET}, 10^8 s^{-1} from $1/\tau$	k_H, 10^8 s^{-1} from Φ	k_{ET}, 10^8 s^{-1} from Φ	Φ_{ET} (%)
Bz-3-ONp	16.3	5.5	13.5	71−86
Bz-4-ONp	4.5	0.4	4.5	92
Bz-5-ONp	3.1	1.9	2.2	54−76
Bz-6-ONp	2.5	1.8	1.8	50−69
Bz-7-ONp	2.0	2.0	1.4	41−59
Bz-9-ONp	3.8	2.1	3.2	60−72
Bz-10-ONp	4.4	2.9	3.0	51−75
Bz-11-ONp	1.7	2.2	1.0	31−53
Bz-14-ONp	1.2	1.5	1.1	46−58
MeBz-3-ONp	23	1.2	22	95−97
MeBz-4-ONp	5.0	0.1	5.0	98
MeBz-5-ONp	3.6	0.3	3.6	92
MeBz-6-ONp	3.1	0.35	3.1	90
MeBz-7-ONp	2.8	0.4	2.7	89
MeBz-11-ONp	2.5	0.5	2.3	86

Table 5. Intramolecular Energy Transfer Rate Constants in Biphenyloxy Ketones

D-n-OA	k_{ET}, 10^8 s^{-1} from $1/\tau$	k_H, 10^8 s^{-1} from Φ	k_{ET}, 10^8 s^{-1} from Φ	Φ_{ET} (%)
Bz-3-O4Bp	7.8	3.9	6.5	62−75
Bz-4-O4Bp	3.5	0.45	3.5	90
Bz-5-O4Bp	2.0	1.1	1.8	62−69
Bz-6-O4Bp	1.6	1.1	1.5	60
Bz-7-O4Bp	1.2	1.5	1.0	40−48
Bz-9-O4Bp	2.5	1.8	2.1	49−64
Bz-10-O4Bp	2.0	0.9	2.5	59−73
Bz-11-O4Bp	1.0	1.9	0.5	21−42
Bz-14-O4Bp	0.7[a]	1.9	0.2[a]	10−33
Bz-3-O3Bp	5.3	3.5	4.4	56−67
Bz-6-O3Bp	1.4	1.3	1.2	50−58
Bz-7-O3Bp	1.6	1.8	1.1	38−55
Bz-9-O3Bp	0.8	1.2	1.0	36−45
Bz-10-O3Bp	1.4	1.9	0.9	32−50
Bz-14-O3Bp	0.8	1.4	0.8	36
Bz-3-O2Bp	4.1	3.4	3.3	49−61
Bz-4-O2Bp	1.8	0.2	2.0	82−91
Bz-5-O2Bp	1.5	1.2	1.3	52−60
Bz-6-O2Bp	2.1	1.3	1.9	61−68
Bz-7-O2Bp	2.4	1.7	2.0	54−65
Bz-9-O2Bp	1.3	1.3	1.4	50
Bz-10-O2Bp	1.9	1.65	1.7	52−58
Bz-11-O2Bp	0.8	1.6	0.6	27−36
Bz-14-O2Bp	0.6	1.5	0.5	28
MeBz-3-O4Bp	8.5	0.6	8.4	94
Bz-3-O-2-O4Bp	4.4	2.9	4.7	58−62

[a] In benzene.

physical decay processes are known to be too slow to compete at all with hydrogen abstraction. The fact that quantum yields for acetophenone formation are at least as large as those for comparably long alkanophenones without the ω-phenoxy group,[24] whose triplets decay only by hydrogen abstraction, verifies this view.

If k_H in a given bichromophore is assumed equal to that in the corresponding ω-phenoxy compound, the intramolecular energy transfer rate constants k_{ET} can be calculated according to eq 1, where τ is the triplet lifetime of the ω-aryloxyketone,

$$k_{ET} = 1/\tau - k_H - k_2[K] \tag{1}$$

k_H is the rate constant for hydrogen abstraction ($1/\tau$ of the corresponding model ketone in Table 1[35]), k_2 is the rate constant for bimolecular quenching by a ground-state bichromophore's aryloxy group (8×10^9 M^{-1} s^{-1} for naphthalene, 3×10^9 M^{-1} s^{-1} for biphenyl),[4] and [K] is the bichromophore concentration. Because aryloxy ketone concentrations were only 0.001 M, bimolecular quenching rates were 1−2 orders of magnitude slower than the intramolecular rates. Thus, bimolecular quenching could be neglected in most of our calculations, except for the longest lived triplets, where it was taken into account. Equation 1 does ignore the possibility that some intramolecular charge-transfer quenching occurs in the triplets of the shorter bichromophores, since naphthoxy and biphenyloxy groups should be better electron donors than phenoxy. In such cases, the calculated k_{ET} value would be somewhat too high.

Rate Constants k_H Calculated from Quantum Yields and Triplet Lifetimes. The quantum yield of the Norrish type II reaction is expressed in eq 2,[36] where Φ_{ISC} is the quantum yield of intersystem crossing and P_{II} is the probability that the

abstraction rate constants (k_H) in bichromophores from these data is crucial for k_{ET} calculations because, provided that there are no other reactions, k_H competes only with energy transfer (Scheme 1). Comparison of the two methods establishes the internal consistency of the data. As Tables 4 and 5 show, the two methods provide slightly different k_{ET} values for a given compound but nearly identical variations with structural change. The two methods are described more fully below.

Rate Constants k_H Obtained Only from $1/\tau$ Values of Model Phenoxy Ketones. The model phenoxy ketones provide values for the quantum efficiencies of product formation and the rate constants for γ-hydrogen abstraction in the absence of triplet energy transfer. Rapid γ-hydrogen abstraction is presumed to be their only triplet reaction, since energy transfer to the phenoxy group is highly endothermic, charge-transfer quenching of triplet phenyl ketones by anisole is slow,[33,34] and all other

(33) Kochevar, I.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859.

(34) Wolf, M. W.; Brown, R. E.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 526.

(35) Since the ω-phenoxy ketones studied did not include all of the *n* values, a few quantum yield and k_H values were interpolated from the measured values of Table 1.

$$\Phi_{\text{II}} = \Phi_{\text{ISC}} k_{\text{H}} \tau P_{\text{II}} \tag{2}$$

biradical will form products rather than revert to starting ketone. Inasmuch as the model ω-phenoxy ketone triplets undergo only γ-hydrogen abstraction, their product quantum yields equal P_{II}. Since all the compounds have the same absorbing chromophore, with $\Phi_{\text{ISC}} = 1$,[20,21] this factor cancels out in all calculations. However, should there be any additional contribution to $1/\tau$ besides $k_{\text{H}} + k_{\text{ET}}$, such as the charge transfer suggested above, it would lower the product quantum yield. The quantum yields thus provide direct information about how k_{H} values may vary between a bichromophoric ketone and its phenoxy model. With Φ_{II}^{o} being the quantum yield for the phenoxyketone, Tables 2 and 3 include k_{H} values derived from eq 3, which must be compared to the $1/\tau$ values in Table 1. The values of k_{H} depend

$$k_{\text{H}} = (1/\tau)(\Phi_{\text{II}}/\Phi_{\text{II}}^{o}) \tag{3}$$

on the nature of the aryloxy group in D-n-OA, especially in those with three and four methylene tethers. It is known that intramolecular abstraction of a γ-hydrogen atom is strongly affected by inductive effects of γ and δ substituents.[23] Thus, the rate constant k_{H} may differ slightly in a bichromophore and its model compound. However, in both cases, k_{H} is largest when $n = 3$ and much smaller when $n = 4$, the former because the aryloxy group weakens the γ C−H bond, and the latter because the aryloxy group slows hydrogen abstraction by its electron-withdrawing character.[23]

The rate constants for energy transfer can be calculated from eq 1 with the eq 3 value of k_{H}. The variations in these k_{ET} values match the trends of the values derived from only lifetime measurements. Their statistical accuracy may not be as high, since each Stern−Volmer experiment consists of 20 independent HPLC measurements while quantum yield experiments involve only four. For that reason, the lifetime-based k_{H} values are plotted in the figures discussed below. Equation 3, like eq 1, still provides too large a value of k_{ET} should any other triplet decay process exist.

It should be noted that the k_{H} values are fairly constant at $(2 \pm 0.5) \times 10^{8}$ s^{-1} when $n > 5$. If k_{q} values decreased as n increased, then the apparent values of k_{H} would also decrease, since triplet lifetimes would then be longer than the tables indicate. Since the value of k_{H} is determined by the local conformations of the $C_{\text{C=O}}-C_{\alpha}$, $C_{\alpha}-C_{\beta}$, and $C_{\beta}-C_{\gamma}$ bonds and since these conformations are little influenced by the length of the remaining chain, the observed near constancy of k_{H} strongly suggests that the triplet lifetimes measured by Stern−Volmer quenching are accurate within a factor of 1.5, and thus that the trends observed in the k_{ET} values are also accurate.

Discussion

Correlation of k_{ET} Values. Figure 1 compares intramolecular TET rate constants for our Bz-n-ONp bichromophores with those for rigid molecules in which the benzophenone donor and the naphthalene acceptor are attached in all-equatorial positions to a cyclohexane or decalin ring[9] or 10 carbons apart on a steroid.[10] Such isomers, with each chromophore *anti* to the skeleton, display through-bond energy transfer rate constants about 10 times higher than those of isomers with substituents in equatorial−axial positions (i.e., *anti−gauche*). These differences presumably reflect the geometric requirements for electronic coupling though σ bonds. In our acyclic compounds, we
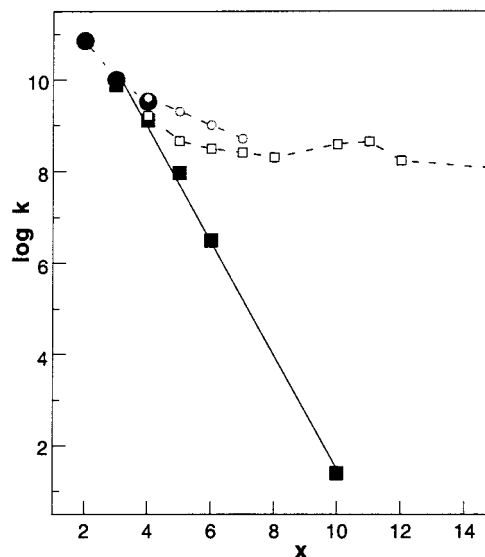
Figure 1. Rate constants for triplet energy transfer as a function of the number x of connecting atoms between the donor and acceptor: ■, PhCOPh-"rigid spacer"-2Np (refs 9 and 10); □, Bz-n-ONp; ●, Bz-$(CH_2)_n$-styryl (ref 13); ○, Bz-$(CH_2)_nCO_2CH_2$-styryl (ref 15).
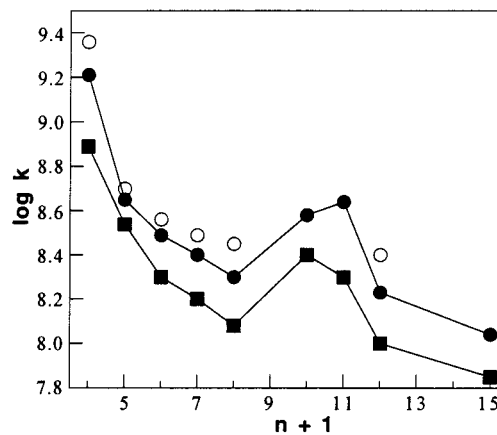
Figure 2. Rate constants for TET as a function of the number of connecting atoms between the donor and acceptor: ▲, Bz-n-ONp; ○, MeBz-n-ONp; ■, Bz-n-O4Bp.

assume that the major conformers have their aryloxy chromophore *anti* to the polymethylene chain. Benzoyl groups often eclipse $C_{\alpha}-C_{\beta}$ bonds,[37] so there should be a significant population of conformers with the benzoyl nearly *gauche* (see Scheme 1). Figure 1 also displays rate constants for two relatively short, flexible benzoyl/styryl bichromophore systems.[13,15]

Figure 2 compares intramolecular TET rate constants for three of our bichromophoric systems, Bz-n-ONp, Bz-n-O4Bp, and MeBz-n-ONp. There are several aspects of the plots in Figure 2 that require separate discussion: the curvature of each plot, with a sharp decrease in the slope as n increases; a bump in the plots for $n = 9-11$; and small differences in k_{ET} as either the donor or the acceptor changes. Since the general shape of the plots is the same for both acceptor chromophores, we shall discuss first how k_{ET} varies with n and then how it varies with chromophore.

Length of the Tether. The shape of the plots in Figure 2 is very different from those associated with covalent bonding[38]

(36) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896.

(37) Wagner, P. J.; Zhou, B.; Hasegawa, T.; Ward, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 9640.

(38) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95.

or excimer and exciplex formation between[39] two functional groups at opposite ends of a molecular chain. This is not surprising, since energy transfer occurs over longer distances than does either covalent bonding or excimer formation. Rate constants for exothermic bimolecular energy transfer between the chromophores used in this work are nearly diffusion controlled.[6,27] The efficiency of correspondingly fast intramolecular processes can be controlled by bond rotation rates and/ or by ground-state conformational distribution.[11,40] Under such conditions, ratios of intramolecular/bimolecular rate constants are not measures of "effective molarity" such as one observes with slow ground-state reactions under conditions of rapid conformational equilibrium.[38] In particular, the k_{ET} values in Tables 4 and 5 are not simple weighted averages over all conformations;[14] thus, we must carefully dissect the various conformational contributions to energy transfer.

Triplet excitation of the carbonyl chromophore is unlikely to significantly alter either the conformational equilibrium or the rotational kinetics of the bichromophoric molecules from their ground-state behavior. Each conformation has its own probability of undergoing energy transfer that depends mainly on the distance between chromophores and their orientations. All conformers whose chromophores are 6 Å or less apart should contribute to the total transfer. Those in which the chromophores are within 3−4 Å of each other should undergo energy transfer in 100 ps or less,[5−7] as observed for *in-cage* bimolecular energy transfer, where chromophores presumably approach van der Waals separation. Whatever small fraction of our aryloxy ketones that preexist in such geometries before excitation would undergo instantaneous energy transfer, since bond rotation would barely compete. Such ground-state control[41] is the intramolecular equivalent of static quenching.[6,11] Likewise, any such geometries formed by bond rotations competing with γ-hydrogen abstraction would also undergo efficient energy transfer so rapidly as to make the bond rotation largely irreversible. Such rotational control is the intramolecular equivalent of diffusion-controlled quenching.[11,40] Conformers with chain ends 5−6 Å apart, where $k_{ET} = 10^8−10^9$ s^{-1},[42] should also contribute directly to the observed value of k_{ET}, but now with efficiencies determined largely by conformational equilibria. Thus, all three kinetics boundary conditions for intramolecular reactions are likely to coexist in our bichromophores, with individual k_{ET} values comprising different combinations of the three.

We include the data for benzoyl-to-styrene TET in Figure 1 to illustrate that, for very short, flexible tethers (3−4 bonds), rate constants are nearly the same as those in Closs's rigid systems, dropping 1 order of magnitude with each additional connecting bond. Likewise, k_{ET} for Bz-3-ONp is nearly identical in value to that for Closs's rigid benzophenone−naphthalene system with five connecting bonds. We might conclude that through-bond interactions predominate in all four-atom (and shorter) tethered molecules, were it not for the strong likelihood of significant population of conformers with gauche attachment of the terminal chromophores in the flexible systems. These presumably would have weaker through-bond interactions,[9] in which case there must be enough through-space interaction to

produce the same overall rate constant. On the other hand, direct connection of the carbonyl to the linking skeleton in our and Cowan's compounds could enhance through-bond coupling relative to that in Closs's systems, in which the connection was para on the benzoyl ring. If there is, indeed, such an enhancement, it does not produce larger k_{ET} values in the shortest flexible bichromophores than those in Closs's analogous compounds, a fact that must reflect how the percentage of gauche conformations increases with x.

In our flexible bichromophores with five-atom links, k_{ET} is lower than that for the corresponding molecules with a four-atom link by a factor of 2−3 but higher by about a factor of 5 than that in the rigid model. The 90% efficiency of energy transfer is a combination of very slow hydrogen abstraction (the inductive effect of δ-alkoxy substitution[23]) and a still relatively high k_{ET}. Molecular flexibility apparently produces sufficient conformations in which the two chromophores are close enough that through-space contributions become competitive with through-bond interaction. Such coiled conformations must contain several gauche C−C bond arrangements, which presumably weaken through-bond interaction but allow through-space interaction.

For flexible bichromophores with $n \geq 5$, the rate constants remain remarkably high, no longer falling an order of magnitude per additional bond as they do for molecules with rigid spacers. In fact, the overall drop on going from $n = 5$ to 14 is a factor of only 0.20−0.25, or 0.86 per bond. (We have too few data for our flexible benzoyl/styrene system[15] to provide a meaningful comparison with the current results.) The rate constants for our longest bichromophores are only 1 order of magnitude lower than those for molecules with four-atom tethers. The rate constant for TET through a rigid steroid molecule in which a benzophenone donor is separated by 11 bonds from a naphthalene acceptor was found to be 25 s^{-1},[10] 7 orders of magnitude smaller than that for our corresponding flexible molecule Bz-9-ONp (3.8×10^8 s^{-1}). Given these huge differences between rigid and flexible spacers, Figures 1 and 2 suggest that >99% of the total energy transfer occurs through space when $n \geq 5$.

From the slow decrease in k_{ET} values as n increases, we conclude that, for molecules with six or more connecting bonds between chromophores, conformational factors produce a nearly constant percentage of coiled geometries in which the two chromophores are close enough for through-space energy transfer to compete with triplet decay, in this case γ-hydrogen abstraction. Similar plateaus have been observed in various studies on electron transfer,[43] spin−orbit exchange interaction in biradicals,[44] and many cyclization reactions.[11,38] Various Monte Carlo calculations[45] as well as exact enumeration calculations of Sisido and Shimada[46] predict that, even for very long molecules with 10−25-atom chains, there exists a certain small fraction of conformations in which the two ends are close enough to interact. What we can conclude is that this small fraction could not produce the observed high energy transfer efficiencies and rate constants.

(39) (a) Zachariasse, K.; Kühnle, W. *Z. Phys. Chem., N. F.* **1976**, *101*, 267. (b) Halpern, A. A.; Legenze, M. W.; Ramachandran, J. *J. Am. Chem. Soc.* **1979**, *101*, 5736.

(40) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461.

(41) Baldwin, J. E.; Kroeger, N. S. *J. Am. Chem. Soc.* **1969**, *91*, 6444. Dauben, W. G.; Williams, R. G.; McKelvey, R. D. *J. Am. Chem. Soc.* **1973**, *95*, 3932. Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6090.

(42) Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1042. Ermolaev, V. L. *Sov. Phys., Dokl.* **1967**, *6*, 600.

(43) (a) Shimada, K.; Shimozato, Y.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 5834 and references therein. (b) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. H.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786. (c) Park, J. W.; Lee, B. A.; Lee, S. Y. *J. Phys. Chem. B* **1998**, *102*, 8209. (d) Staerk, H.; Busmann, H. G.; Kühnte, W.; Treichel, R. *J. Phys. Chem.* **1991**, *95*, 1907.

(44) Forbes, M. D. E.; Closs, G. L.; Calle, P.; Gautam, P. *J. Phys. Chem.* **1993**, *97*, 3384. Forbes, M. D. E.; Schulz, G. R. *J. Am. Chem. Soc.* **1994**, *116*, 10174.

(45) Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. *J. Am. Chem. Soc.* **1992**, *114*, 3285. Avdievich, N. I.; Forbes, M. D. E. *J. Phys. Chem.* **1995**, *99*, 9660. Werner, U.; Staerk, H. *J. Phys. Chem.* **1993**, *97*, 9274.

(46) Sisido, M.; Shimada, K. *J. Am. Chem. Soc.* **1977**, *99*, 7785.

Scheme 3. D-9-OA
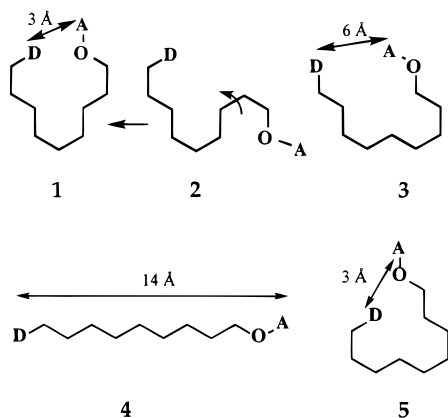
The quantum efficiency of energy transfer in our longer bichromophores (30–60%) is much higher than the expected[44–46] few percent of ground-state conformations with the two ends close enough (3–4 Å) to interact in ≤100 ps. Therefore, only a few percent of the total energy transfer can be attributed to static quenching in this small fraction of the ground-state conformational distribution. The major portion of the energy transfer must be provided by a combination of other conformers irreversibly rotating into such static quenching geometries within the lifetime of the triplet ketone and by conformationally equilibrated conformers with their ends 5–6 Å apart undergoing direct energy transfer with rate constants of 10^8–10^9 s^{-1}. Both of these processes are controlled by rapid conformational interconversion, with bond rotations being rate determining in the former case and energy transfer in the latter. The overall efficiency of energy transfer thus is determined by a combination of ground-state control, rotational control, and conformational equilibrium, as suggested above. The k_{ET} values in the tables are only apparent rate constants that must be apportioned into three components on the basis of what fraction of the overall quantum yield of energy transfer each contributes.

As useful as Monte Carlo calculations are in estimating conformational distributions, it is the dynamics of conformational change that must be understood. For the moment, we can merely offer Scheme 3 to portray, with five representative conformations of a bichromophore connected by a nine-carbon chain, various examples of the above conditions. In what is probably the lowest energy but most sparsely populated conformation, the totally stretched **4**, the donor and the acceptor are about 14 Å apart and cannot undergo internal energy transfer. Likewise, there are scores of conformers with one or two gauche twists that do not bring the two chromophores close enough to interact in the 10-ns lifetime of the triplet carbonyl. In both **2** and **3**, energy transfer can compete with hydrogen abstraction. **3** depicts one conformer with three gauche twists that produce a 6-Å D–A distance, which corresponds to an energy transfer rate constant of ~10^8 s^{-1}. Four gauche twists can produce a conformation such as **1** that, with a 3-Å D–A distance, presumably undergoes energy transfer in ≤100 ps, or one such as **2**, in which irreversible rotation along one C–C bond can bring the acceptor as close to the donor as in **1**. As discussed above, the key necessity for efficient energy transfer is that rates for rotation of unreactive geometries such as **4** and **2** into ones such as **1**, and for establishing equilibrium populations of ones such as **3**, be appreciably faster than the rate of hydrogen abstraction by the triplet benzoyl, i.e., ≥10^9 s^{-1}. The special

case **5** shows a typical low-energy "W" conformation,[38,47] in which donor and acceptor are not in close proximity and/or their orientations are not favorable. However, a through-space (solvent) energy hop from the chromophore to a chain atom (eventually from chain to chain) might contribute to the total energy transfer. The transfer rate constant is assumed to be high because the total transfer path is about 4.5 Å. Calculations of electronic coupling in rigid systems using ab initio MO theory have revealed that paths involving hops which skip over bonds can make the largest contribution to the total through-bond coupling.[48,49]

Equation 4 describes how the quantum yield of energy transfer depends on the three independent kinetic pathways, with

$$\Phi_{ET} = \Phi_{ISC}[\chi_3 + \chi_5(k_{ET}^5 + k_{rot}^5)/(k_{ET}^5 + k_{rot}^5 + k_H) + \chi_u k_{rot}^3/(k_{rot}^3 + k_H)] \quad (4)$$

χ_3 equaling the percent population of ground-state conformers with the two end chromophores 3–4 Å apart, χ_5 equaling the equilibrium population of conformers with the two end chromophores 5–6 Å apart, k_{ET}^5 equaling the average rate constant for energy transfer by that group of conformers, k_{rot}^5 equaling the average rate constant for rotation by that group of conformers to one with the two ends 3–4 Å apart, χ_u equaling the major fraction of the conformers with their ends too far apart to interact, and k_{ET}^3 equaling an average rate constant for these unreactive conformers to rotate irreversibly into ones with their ends 3–4 Å apart. Although k_H certainly depends on ketone conformation, its value does not vary much since the geometry near the carbonyl is relatively fixed in alkanophenones of all lengths (Scheme 1).

We have already noted that ground-state-controlled static quenching (the first term in brackets) contributes, at most, a few percent to the quantum yield, so that the k_{ET} values are comprised mainly of $\chi_5 k_{ET}^5 + \chi_u k_{rot}^3$, each of which represents a weighted average over all appropriate conformations. Given the large number of conformations possible in these molecules, we cannot assess the contributions of the two kinetic processes dependent on conformational interconversion with any accuracy. If it were 50:50, we would have to conclude an average rate constant of ~10^8 s^{-1} for irreversible rotation by something like 70% of the molecules into ones with the ends 3–4 Å apart and about a 30% equilibrium population of conformers 5–6 Å apart that can undergo energy transfer in 1–10 ns.

The behavior of Bz-3-O-2-O4Bp emphasizes the importance of conformational factors, its k_{ET} value being 3 times higher than that of Bz-6-O4Bp, which also has a seven-atom tether. As has often been demonstrated,[43d,50] replacing a methylene group with an oxygen atom reduces gauche torsional strain and thus increases chain flexibility and coiling.

The 2–3-fold jump in energy transfer rates for both Bz-x-O-2Np and Bz-x-O-4Bp with 10- and 11-atom links in Figure 1 represents a major difference between this and some intramolecular electron transfer reactions. This phenomenon will be discussed more fully below, since the behavior of the isomeric biphenyloxy acceptors may offer an explanation.

(47) Goodman, J. M.; Hoffmann, H. M. R.; Vinter, J. G. *Tetrahedron Lett.* **1995**, *36*, 7757. Vinter, J. G.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1974**, *96*, 5466.

(48) Chattoraj, M.; Bal, B.; Closs, G. L.; Levy, D. H. *J. Phys. Chem.* **1991**, *95*, 9666. Chattoraj, M.; Paulson, B.; Shi, Y.; Closs, G. L.; Levy, D. H. *J. Phys. Chem.* **1993**, *97*, 13046.

(49) Mutz, M. W.; McLendon, G. L.; Wishart, J. F.; Gaillard, E. R.; Corin, A. F. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 9521.

(50) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 3702.

Scheme 4
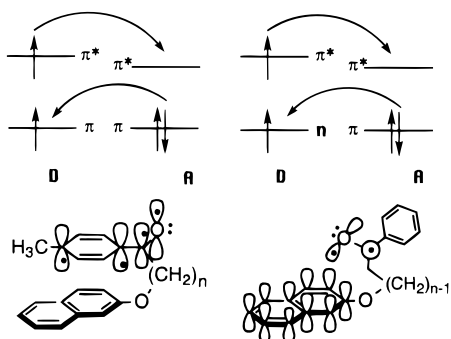
Electronic Factors. The measured k_{ET} values for 4-biphenyl acceptor are consistently lower by a factor of ~2 than those for the naphthyl acceptor, although both systems exhibit the same profile for the dependence of k_{ET} on tether length. Since the length of a 2-naphthyl group resembles that of 4-biphenyl, as will be discussed below, electronic effects seem to be the only factors causing differences in behavior of these two bichromophores. It is known that the lowest energy conformation of the biphenyl ground state in solution is twisted, while in the T_1 state the two rings are coplanar.[51] This conformational change in biphenyl slows energy transfer because of unfavorable Franck−Condon factors, as was shown in both bimolecular[4,51a] and intramolecular energy transfer[52] studies. Combining our current results with the earlier ones indicates that this effect is independent of whether through-bond or through-space interaction predominates. Discussion below of the 2- and 3-biphenyl-oxy acceptors elaborates on this phenomenon.

Energy transfer rate constants are higher by a factor of roughly 1.5 for all tether lengths when a 4-methylbenzoyl (*p*-toluyl) group rather than a benzoyl group is the donor. The difference is small but consistent, and a shift from through-bond to through-space mechanism obviously does not play any role in this case. We studied the *p*-toluyl donor to determine the extent to which different electronic configurations of the donor influence energy transfer rates, since the lowest triplet state of phenyl alkyl ketones is n,π^*, while that of *p*-tolyl alkyl ketones is π,π^*,[25] with only some 10% population of their upper n,π^* triplet.[26] Whereas the two singly occupied molecular orbitals (SOMOs) of n,π^* ketone triplets are heavily localized on the carbonyl group,[53] π,π^* excitation is centered primarily on the benzene ring.[54] That the different electronic distributions of the two states greatly affects rates of hydrogen transfer is well known[25b,26,55] and is reflected in the k_H values in the tables. Scheme 4 depicts our expectation for the likely difference in molecular geometries for efficient energy transfer from π,π^* and n,π^* donors, based on the concept of two one-electron transfers between highest occupied molecular orbitals and lowest unoccupied molecular orbitals. Despite the slightly greater exothermicity for energy transfer from an n,π^* triplet, two major factors would suggest slower energy transfer from the n,π^* state. First, whereas the acceptor π and π^* orbitals are parallel, the donor n and π^* orbitals are orthogonal. Energy transfer would appear to require
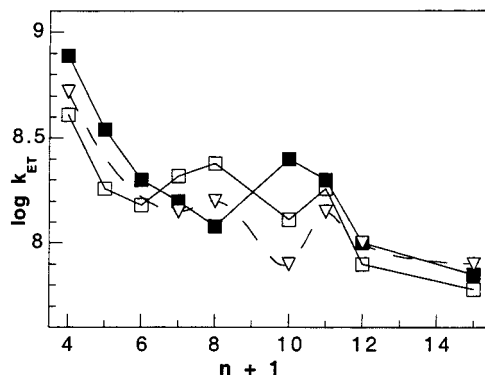
Figure 3. Rate constants for triplet energy transfer, k_{ET}, as a function of the number of atoms connecting the donor and the acceptor: ■, Bz-*x*-O4Bp; ▽, Bz-*x*-O3Bp; □, Bz-*x*-O2Bp.

a change of orbital orientation during the process, experimental evidence for which occurs in the negative ΔS for excitation of benzophenone.[56] Second, efficient overlap of the half-occupied oxygen n orbital with the acceptor's π system requires a different geometry for both the tether and the ketone function than that required for simple parallel overlap of donor and acceptor π systems.[57] (These same orbital geometry expectations often have been used to analyze charge-transfer reactions of triplet ketones with aromatic donors.[34,58]) Nevertheless, the difference between benzoyl and *p*-toluyl donors was found to be very small. This finding might suggest that there is little energy difference between the connecting chain geometries required for efficient n or π overlap of ketone with acceptor and/or that efficient electron exchange can occur with less than ideal orbital orientations, as Ghiggino[59] and Levy[60] have suggested. However, the effect of orientational factors on those portions of the intramolecular energy transfer that are static or rotationally controlled would be diminished by the rapidity of short-range energy transfer compared to bond rotations; only the slower TET in conformationally equilibrated molecules could show any dramatic effect.

Isomeric Differences. Figure 3 compares the behavior of the three bichromophoric systems with 4-, 3-, and 2-biphenyloxy acceptors, the three resulting plots of k_{ET} vs $n + 1$ each having rate jumps at longer n values, as observed for the 2-naphthoxy compounds, but with maxima at different n values such that the relative rate constants for the three isomers vary considerably with n.

The compounds with 4−6-atom tethers display normal descending reactivity as n increases, with the para isomer reacting twice as fast as the ortho, and the meta in between. The barrier to rotation of an ortho substituent on biphenyl is significantly higher than those for meta and para substituents due to steric interference with the other ring.[61] Likewise, the change from twisted ground state into coplanar triplet in the 2-biphenyloxy group is more energetically difficult than in the other isomers,[62] and Franck−Condon factors slow energy

(51) (a) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820. (b) Hutchison, C. A., Jr.; Kemple, M. D. *J. Chem. Phys.* **1979**, *71*, 866. (c) Takei, Y.; Yamaguchi, T.; Osamura, Y.; Fuke, K.; Kaya, K. *J. Phys. Chem.* **1988**, *92*, 577.
(52) Sigman, M. E.; Closs, G. L. *J. Phys. Chem.* **1991**, *95*, 5012. Miller, J. R.; Paulson, B. P.; Bal, R.; Closs, G. L. *J. Phys. Chem.* **1995**, *99*, 6923.
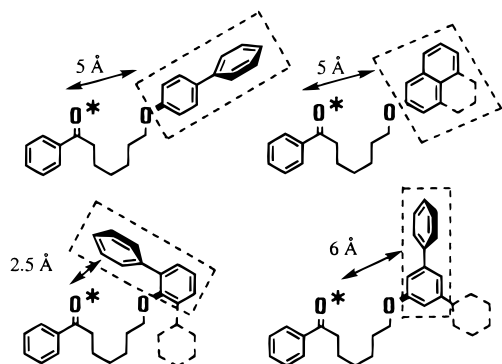(53) Hochstrasser, R. M.; Scott, G. W.; Zewail, A. H. *Mol. Phys.* **1978**, *36*, 475.
(54) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7335.
(55) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(56) Gessner, F.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7206.
(57) Mirbach, M. F.; Ramamurthy, V.; Mirbach, M. J.; Turro, N. J.; Wagner, P. J. *Nouv. J. Chim.* **1980**, *4*, 471.
(58) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.
(59) Harcourt, R. D.; Ghiggino, K. P.; Scholes, G. D.; Speiser, S. *J. Chem. Phys.* **1996**, *105*, 1897.
(60) Yip, Y. T.; Levy, D. H.; Kobetic, R.; Piotrowiak, P. *J. Phys. Chem. A* **1999**, *103*, 10.
(61) Katritzky, A. R.; Topsom, R. D. *Chem. Rev.* **1977**, *77*, 639. Topsom, R. D. *Acc. Chem. Res.* **1983**, *16*, 292. Wolf, C.; König, W. A.; Roussel, C. *Liebigs Ann. Chem.* **1995**, 781.
(62) Scheve, B. J.; Wagner, P. J. *Chem. Phys. Lett.* **1974**, *25*, 324.

Scheme 5

Figure 4. Rate constants as a function of the number of bonds connecting the donor and acceptor: ●, triplet energy transfer in Bz-n-ONp; electron transfer in □, pyrene-$(CH_2)_n$-dimethylaniline (ref 43d), ○, anthracene-CO_2-$(CH_2)_n$-NMe$_2$ (ref 64), and △, phthalimide-$(CH_2)_n$-phthalimide$^{•-}$ (right Y axis, ref 43a).

transfer even more, as we showed years ago.[63] On the other hand, ortho and especially para alkoxy groups stabilize a planar biphenyl conformation by increasing the electron density at the carbon in the pivot bond, thus decreasing the rotational energy barrier by resonance.[61] We conclude that the 2-biphenyloxy acceptor shows lower energy transfer rates because of steric crowding and that the 4-biphenyloxy acceptor produces the highest rate constants because of a resonance effect that is absent in 3-substituted biphenyls. The behavior of the longest bichromophores (12- and 15-atom tethers) is comparable in that k_{ET} values are nearly the same for all three isomers. However, the situation for molecules with tethers of medium length is much more complex. In the region of 7−11-atom tethers, Bz-n-O4Bp shows a single rate constant jump for $n = 8−10$, whereas Bz-n-O3Bp and Bz-n-O2Bp show two such humps, one maximized at $n = 7$ and one at $n = 10$. These anomalies result in an ortho > meta > para rate constant ratio at $n = 7$ and a para ≈ ortho > meta ratio at $n = 10$.

All four acceptors show a rate jump maximized at $n = 9$ or 10, while only the two with 2- and 3-biphenyloxy acceptors show an additional jump at $n = 7$, which amounts to a 4-fold jump in the ortho/para rate ratio and a 2-fold jump in the meta/para ratio. Scheme 5 presents a possible explanation for the $n = 7$ jump based on the outcome of a single bond rotation in a single chain conformer. The four acceptors are compared in terms of a "reactive volume" originating from the rotation. The scheme exemplifies how rotation about the C−O bond of a single D-6-OA conformation affects the distance between the far ring of the acceptor and the carbonyl oxygen. The position of the phenyl ring attached to oxygen is not influenced by the rotation and is identical for all four acceptors. The more distant phenyl in the 4-biphenyl and 2-naphthyl chromophores obviously gets little closer to the carbonyl donor during the rotation and so cannot enhance energy transfer. Rotation of the 3- and especially 2-biphenyl groups does, however, cause the more distant ring to approach the donor carbonyl close enough to promote more efficient energy transfer. For both the 2- and 3-biphenyloxy acceptors, in one favorable chain conformation half of the C−O rotamers position the distal phenyl ring closer to the carbonyl than can occur with the 4-biphenyloxy acceptor. Of course, the overall rate effect is too large to be explained by a single conformer. We conclude that, in the torsionally challenged medium-ring chains, there are significant populations of such geometries in which the orientation of the second phenyl ring in the biphenyls has a large effect on energy transfer, whereas no such effect that can be explained by a C−O rotation manifests itself for either the short molecules or the very long ones.
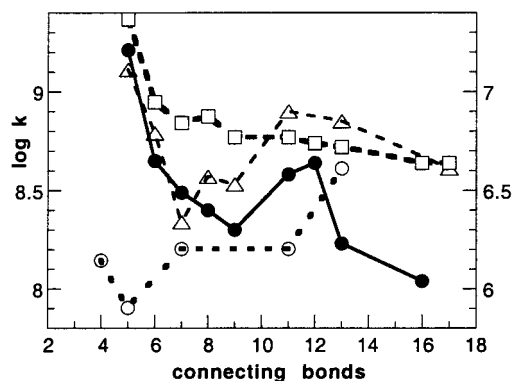
We have not explained the rate jumps at $n = 9−11$, which obviously have nothing to do with rotations around the terminal acceptor−chain bond. Two possible reasons come to mind. There may be a larger percentage of chain conformations that allow close approach of the chain ends when $n = 9$ or 10 than when $n > 11$. Alternatively, we could consider the minimum at $n = 7$ for the naphthoxy and 4-biphenyloxy acceptors to be the normal effect of forming medium-sized rings, which is offset by favorable rotamers of the other biphenyloxy isomers, as just explained. In that case, the rise in rates as n approaches 10 would also be normal, but the drop in rates for larger n would require a new explanation for how increasing chain length affects the dynamics and thermodynamics for bringing the two ends close enough to interact.

Comparison with Electron Transfer. Given the similar exchange interactions responsible for both energy and electron transfer, one might expect a resemblance between our plots in Figure 2 and comparable plots of electron transfer. Figure 4 compares our results with three such investigations of electron transfer between donors and acceptors connected by a polymethylene chain: electron exchange between two phthalimide groups[43a] and electron transfer from a dimethylamino group to an excited singlet anthracene[64] and from dimethylaniline to excited singlet pyrene.[43d] It is interesting that none of the three have remotely similar profiles, the thermoneutral one showing the same bump at 11−12 bonds as ours. The variability in the shapes of such plots for rates of intramolecular covalent bonding is ascribed to varying orientational requirements for the actual transitions state for bonding;[38] both electron and energy transfer may be subject to variable orientational requirements. Electron-transfer rates in the pyrene-$(CH_2)_n$-dimethylaniline system[43d] provide a plot similar to ours but without any significant hump. Since that study was performed in acetonitrile, we suspect that the essentially constant k_{ET} value of (5−6) × 10^8 s^{-1} for $n = 8−16$ represents extensive solvent-induced chain coiling, which could mask normal conformational effects as well as enhance through-space interactions beyond those derived from solvent-independent conformations.

Summary

This study presents a very consistent picture that shows that intramolecular triplet energy transfer in flexible molecules is dominated by through-space/-solvent interactions when the

(63) Wagner P. J.; Scheve, B. J. *J. Am. Chem. Soc.* **1977**, *99*, 2888.

(64) Vanderauwera, P.; DeSchryver, F. C.; Weller, A.; Winnik, M. A.; Zachariasse, K. A. *J. Phys. Chem.* **1984**, *88*, 2964.

connecting tether contains five or more bonds, since rate constants for energy transfer are decreased by a factor of only 0.86 for every additional intervening C−C bond, in contrast to the factor of 0.1 observed for systems with rigid cycloalkane spacers between donor and acceptor. Thus, the compound Bz-$(CH_2)_{14}$ONp, with a 15-atom tether, undergoes internal triplet energy transfer 10% as rapidly as does Bz$(CH_2)_3$ONp, which presumably operates primarily by through-bond energy transfer. Exchanging one CH_2 group with an oxygen atom increases k_{ET} by a factor of 3, a result that stresses the importance of conformational dynamics of the connecting chain in maintaining a significant fraction of molecules in coiled geometries with their ends close enough for electron exchange to compete with the γ-hydrogen abstraction that occurs in each of the molecules.

The bumps in the k_{ET} vs n plots for the 2- and 3-biphenyloxy acceptors at $n = 7$ accentuate the importance of short end-to-end polymethylene chain distances, since it is only in such geometries that rotation around the O-biphenyl bond can produce carbonyl−biphenyl distances shorter than possible for the para isomer. The bump at $n = 10$ or 11 for all acceptors cannot have similar close end-to-end approaches as an explanation and so may, in fact, merely reflect the normal drop in rate constants for formation of medium-sized 8−10-carbon rings, offset by the differences in the isomeric biphenyl acceptors, plus a drop-off in the availability of sufficiently close end-to-end approach as n increases beyond 11.

Energy transfer to 4-biphenyl acceptors is slower than that to naphthyl, as previously shown for both bimolecular and intramolecular quenching of triplet ketones. This study shows that the 2−3-fold rate decrease caused by the change in coplanarity of the two rings of biphenyl is of the same size for both through-bond and through-space energy transfer, as expected for a purely electronic effect.

Comparison of rate constants for *p*-toluyl and benzoyl as triplet donors indicates that the $\pi,\pi*$ triplet of the former transfers energy only 1.5 times faster than does the n,$\pi*$ triplet of the latter. This result is most interesting in view of the orthogonality of the relevant SOMOs in the n,$\pi*$ triplet; there do not appear to have been any other such measurements.

These results furnish only a semiquantitative picture of how connecting chain length affects energy transfer rates. Higher level calculations are necessary for a more complete understanding of both conformational dynamics and thermodynamics in such systems.

Experimental Section

Solvents. Reagent grade benzene (J. T. Baker) was washed with sulfuric acid until further portions remained colorless and then washed, dried, and distilled over P_2O_5, bp 80 °C. Reagent grade cyclohexane (CCI) was washed with sulfuric acid until further portions remained colorless and then washed, dried, and distilled over CaH_2, bp 81 °C.

Quencher. 2,5-Dimethyl-2,4-hexadiene (Aldrich) was allowed to sublime in a refrigerator.

Actinometers and Standards. Acetophenone, 4-methylacetophenone, methyl benzoate, valerophenone, and 4-methylvalerophenone were all commercially obtained materials (Aldrich) and were purified by fractional distillation before use.

ω-Aryloxy Ketones. These were all synthesized, characterized, and purified by following standard procedures, as described in the Supporting Information.

Analytical Procedures. ^{1}H and ^{13}C NMR spectra were obtained on either a 300-MHz Varian Gemini or a 300-MHz Varian VXR-300 instrument. IR spectra were recorded on a Nicolet IR/42 Fourier transform IR spectrometer, and samples were prepared using a pressed KBr disk technique. UV spectra were recorded on a Shimadzu UV-160 spectrometer with matched 1.0-cm quartz cells. High-resolution mass spectra were obtained on a Joel JMS-HX110 double-focusing mass spectrometer in the MSU Mass Spectroscopic Facility: the electron impact and direct probe methods usually were used. Melting points (uncorrected) were measured on a Thomas-Hoover capillary melting point apparatus. HPLC analyses were performed on either a Rainin HPXL apparatus equipped with a Dynamax UV-D absorbance detector or a Dynamax SD-200 system equipped with a PDA-1 Dynamax diode array detector, in both cases with a normal-phase Rainin Microsorb Si80-125-CS silica gel column and a 100-μL loop.

Identification of Photoproducts. The only photoproducts common for all reactants in this work were acetophenone and 4-methylacetophenone. Their identification was based on ^{1}H NMR, ^{13}C NMR, and HPLC comparisons with authentic samples (Aldrich).

Photokinetic Measurements. Irradiation procedures were as in earlier work.[14] Samples of known concentrations were prepared: 2.8-mL aliquots were placed in 13- × 100-mm Pyrex tubes that were then degassed in three freeze−pump−thaw cycles before being sealed. Samples were irradiated in a "merry-go-round" apparatus[65] immersed in a water bath. The 366-nm band from a medium-pressure 450-W Hanovia mercury arc lamp was isolated by filtration with Corning 7-83 filters. Samples were analyzed by HPLC with response factors for products and methyl benzoate internal standard calibrated with authentic samples. Parallel irradiation of 10^{-3} M valerophenone solutions, where the quantum yield of acetophenone production is 0.30,[22] provided actinometry.

Supporting Information Available: Synthesis and characterization of all the ω-aryloxyalkyl phenyl ketones (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(65) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.