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ENANTIOTOPIC INTERACTIONS IN THE FLUORESCENCE QUENCHING OF CAMPHOR BY CHIRAL AMINES

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A study of the quenching of fluorescence of (+)- and (-) camphor in hexane by a series of chiral primary, secondary, and tertiary amines shows only very small differences in quenching rate constants for the two enantiomers. The collision complex which precedes quenching (probably charge transfer) is thus insufficiently tight for enantiomeric recognition.

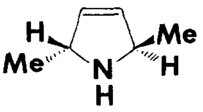
Recent interest[1] in identifying the geometries required for efficient excited state bimolecular interaction prompts us to report our observations on the rates of fluorescence quenching of (+) and (-) camphor with a family of chiral amines. By employing both chiral excited molecules and chiral quenchers, it should be possible to more clearly examine pure steric interactions without the complicating electronic and solvation changes that accompany less subtle geometric probes.

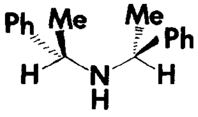
The recognition within the last decade that molecular association in the excited state is often significantly more important than in the ground state[2] has led to widespread investigations of both ground state molecular complexes[3] and their excited state counterparts.[4] Many excited state bimolecular reactions are believed to occur by charge-transfer, excimer or exciplex intermediates.[4]

The chemistry of exciplexes and charge-transfer intermediates formed by the interaction of amines with aromatic hydrocarbons and with carbonyl compounds has been particularly well studied. In non-polar solvents, tertiary amine-aromatic hydrocarbon exciplexes are often strongly fluorescent[2] and frequently undergo reduction or addition reactions in polar solvents, presumably via charge-transfer radical ion pairs.[5] Secondary amine-aromatic hydrocarbon exciplexes give even more rapid addition and reduction, presumably because of the facility of rapid proton transfer from secondary amines.[6] Analogous charge-transfer interactions, often accompanied by reduction and/or addition, have often been observed in amine-ketone photochemistry.[7,9]

Little definitive information is available, however, on the geometric requirements for the formation of amine/ketone exciplex or charge-transfer intermediates. The existence of two types of excimer fluorescence from dianthrylethylenes led Mataga and coworkers to suggest two distinct excimer conformations.[8] Inconclusive evidence has also suggested multiple conformations for ground state charge transfer complexes.[2] Dalton and Snyder[7e] have shown that alkyl ketone fluorescence quenching probably occurs by electron transfer (i.e., via a charge-transfer complex) and that the rate of such quenching is slowed by increasing methyl substitution near the carbonyl site. Such quenching effects could be steric and/or inductive in origin.

We have reasoned that if conformation or steric bulk is a prime determinant of exciplex chemical reactivity, the rate of formation of the exciplex (and hence the rate of monomer fluorescence quenching of one partner of the exciplex by the other) should differ significantly when each of the two possible enantiomers of an optically active molecule forms an exciplex with a chiral partner. Since the photoreaction of ketones with aliphatic amines is believed to proceed through singlet and/or triplet exciplexes[7,9] and/or charge-transfer intermediates,[7e,10] we have examined the kinetics of the fluorescence quenching of (+) and (-) camphor (1) by a series of chiral amines to determine if the singlet encounter complex was sufficiently tight to kinetically distinguish enantiomers. The amines employed were (-)-trans-2,5-dimethylpyrrolidine (2),[11] (-)-SS-N-(1-phenylethyl)-1-phenylethyl amine (3)[12] (+) and (-)-1-phenylethyl amine (4),[13] (+) and (-)-N-methyl-1-phenylethyl amine (5),[14] and (+) and (-)-N,N-dimethyl-1-phenylethyl amine (6).[9]


(-)-2


(-)-3

The fluorescence at 420 nm of a solution of (+) or (-) camphor[16] in spectral grade hexane (ca. 3×10^{-2} M) was monitored as quantities of amine were incrementally added ($0\text{-}30\times10^{-2}$ M). Excellent linear plots of the camphor fluorescence intensity ratio (Io/I) vs. the concentration of added amine were obtained, the slopes of which gave kq τ. Since the singlet lifetime of camphor is known[7e] such plots can directly give kq, the amine quenching constant. The results obtained by this standard Stern-Volmer treatment are listed in Table 1.

Table 1. Fluorescence Quenching of Camphor by Chiral Amines

Amine[d]	kq[b][(+)-1]x10^{8}	kq[(+)-1]/kq (-)-1
(-)-2	16(± 2)	0.97 ± (0.05)
(-)-3	4.8	1.10
(+)-4	4.5	0.91
(-)-4	5.2	1.00
(+)-5	10[c]	0.91
(-)-5	10[c]	1.02
(+)-6	12[c,e]	1.00
(-)-6	13	1.02

a) Excitation of 1 at 300 nm; Emission monitored at 420 nm; Minor fluorescent impurities accounted for <2% of total fluorescence.

b) Average of three-five kinetic determinations.

c) Single determination.

d) Optical purities >95%.

e) Corrected for the presence of a significant fluorescent inpurity.

As in previous studies,[7] we observe that the quenching rates are lower than the rates of diffusion. Thus, fluorescence quenching represents only one competing path available to such an amine/ketone encounter complex.

Our observed differences in kq for chiral amines with (+)- and (-)-1 are small. The size of the differences, if real, are reminiscent of the low optical yields usually achieved in photoinduced asymmetric induction[17] from exciplexes and are smaller than the enantiomeric quenching differences observed by Ire et al. in amine/aromatic hydrocarbon encounter complexes.[1] We conclude that in our fluorescence quenching experiments enantiomeric interactions in the excited singlet states, whether as exciplex, charge-transfer intermediate or collision complex may be real, but that such steric interactions probably cannot be the sole determinants of the efficiency of excited state bimolecular quenching. Our results thus suggest that excited state quenching interactions can occur through some spatial separation within the encounter complex.[18] The ability to achieve asymmetric induction via exciplex interactions can probably not be generalized, but will differ from one system to another, depending on the spatial separation within the encounter complex.

A more complete description of the photophysics of the exciplexes formed by amines 2 and 3 will be given elsewhere.

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