Photophysical Studies on Molecular Chirality: Ground and Excited State Enantioselective Interactions between 2-Naphthyl-1-ethanol and Natural Bicyclic Compounds

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Jet-cooled isolated diastereoisomeric pairs formed between *R*- and *S*-2-naphthyl-1-ethanol and a series of optically active terpenes have been investigated by studying both the fluorescence excitation spectra and the fluorescence decays. While the homo- and heterochiral complexes with α-pinene and borneol can be resolved spectrally, no spectral enantiodifferentiation was obtained in the case of camphene and camphor complexes. Chirality-dependent fluorescence decays were however observed for these complexes which exhibit either longer lifetimes than the bare chromophore for the diasteroisomers involving camphene, or shorter for those with camphor. The enantioselective quenching of fluorescence of 2-naphthylethanol by *R*- and *S*-camphor has also been observed in *n*-hexane solution and has been shown to be due to a singlet−singlet energy transfer taking place at a rate lower than diffusion. In contrast, the energy transfer to *R*- and *S*-camphorquinone and biacetyl was shown to be diffusion controlled and nonenantioselective.

Introduction

The development of new methods for the characterization of chiral species represents a challenging area from the analytical point of view for resolution of enantiomers as well as for the understanding of the intrinsic factors responsible for the enantioselectivity.

The discrimination between optically active isomers commonly observed in life chemistry relies on the ability of a natural compound of a given chirality to interact in a stereospecific manner with a set of enantiomers. Accordingly, most of the analytical methods developed in this domain mimic nature and use a chiral reagent to convert the mixture of enantiomers into diastereoisomers.[1] Our previous studies on chiral recognition by spectroscopic means rest on the same principle and take advantage of the capability of supersonic expansions to produce weakly bound clusters under isolated gas-phase conditions.[2,3] By using a chiral chromophore (2-naphthyl-1-ethanol, 2-NetOH) in the presence of chiral alcohols, the enantiospecific complexation resulting from the association of the nonequivalent R−R (S−S) or R−S (S−R) chiral pairs has been probed by laser-induced fluorescence techniques. The different spectral signatures obtained for the diastereoisomers allow us to clearly distinguish between them and demonstrate the potentiality of the method.

However, it has been observed that the fluorescence excitation spectra of chiral pairs appear to be not as simple as one would expect since they present in most cases numerous features in the region of the origin of the S_0-S_1 transition even for pure enantiomeric mixtures. This complexity can be understood because the molecules under study are quite flexible and can exist in different conformations at the low internal temperature obtained by supersonic cooling. Indeed, it has been further shown from ground state depletion experiments that in the case of complexes involving simple secondary alcohols such as 2-butanol or a primary alcohol such as 2-methyl-1-butanol each diastereoisomer can exist in two isomeric forms that involve two different conformations of the solvent.[4] Calculations based on the exchange perturbation method performed on the same systems indicate that two types of interactions are dominant: hydrogen bonding between the OH group of the 2-naphthyl-1-ethanol and the oxygen of the solvent alcohol, which is electrostatic in nature, and the dispersive interactions between the alkyl chain of the solvent and the aromatic ring of the chromophore. This latter type of interaction is responsible for the red shift of the probed transition and is thought to be determinant for the observed enantiodifferentiation.

This study constitutes a new part of our ongoing work on chiral recognition in van der Waals complexes under isolated gas-phase conditions. The chiral systems investigated involve the same chiral selectand as previously: 2-naphthyl-1-ethanol (2-NetOH) in interaction with rigid bicyclic compounds such as terpenes (α-pinene, camphene) and related compounds (camphor and borneol) (Chart 1). The first part of the paper is devoted to the investigation of the isolated complexes formed in the supersonic expansion by laser-induced fluorescence with the aim to give further insight to the enantioselectivity both on a spectroscopic and a dynamical point of view. While the excitation spectra of the hetero- and homochiral complexes of 2-NetOH with α-pinene and borneol exhibit a different shift of the S_0-S_1 transition of the excited chromophore, no differences have been obtained for camphene and camphor. However, a chirality-dependent effect was evidenced in all diastereoisomers from lifetime measurements. The 1:1 complex with camphor[5] which has been previously characterized by two-color REMPI experiments exhibits a drastic quenching of the chromophore fluorescence in the case of the homochiral pair and a slight change in the case of the heterochiral pair. Because of this large difference, it was anticipated that enantioselective quenching can also be observed in solution and the chirality dependence of the fluorescence of the naphthyl chromophore in the presence of camphor and camphorquinone in solution was examined in the second part of the paper.

Experimental Section

Chemicals. 2-Naphthyl-1-ethanol and the complexing bicyclic compounds are obtained either in their optically active pure

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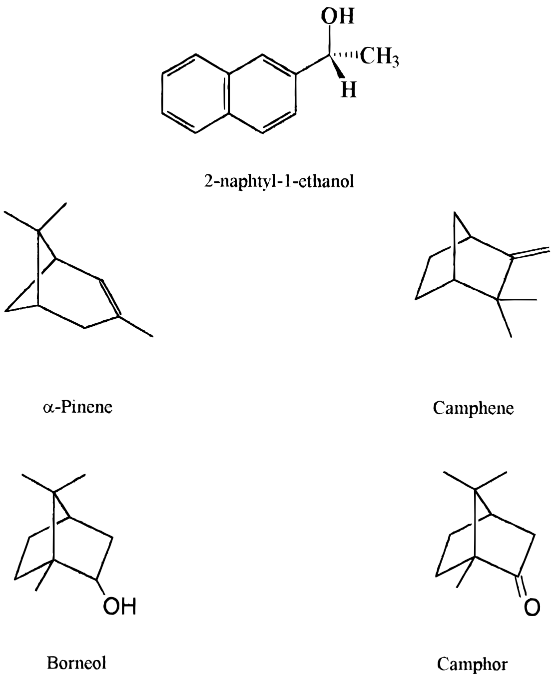
CHART 1. Structure of 2-Naphthyl-1-ethanol and the Chiral Terpenes Used for Complexation



forms or in racemic mixtures from Aldrich and used without further purification. *n*-Hexane (Uvasol quality) from Merck was used for the experiments in solution.

Jet Experiments. The experimental set up has been described elsewhere.[2] Briefly, it consists of a continuous supersonic expansion obtained by pumping a helium flux at 2 atm backing pressure through a 200 μm nozzle into a vacuum chamber pumped at 10^{-3} Torr. The helium carrier gas is seeded with the vapor pressure of the 2-NetOH chromophore contained in a small reservoir heated at 90 °C and located just before the nozzle. The bicyclic additives situated in another independent reservoir upstream are also heated prior to the expansion to provide enough vapor pressure. The species present in the cold zone of the jet are excited perpendicularly to the jet axis by a frequency doubled (KDP) dye laser (DCM) pumped by the second harmonic of a YAG laser (Quantel). The fluorescence signal observed directly through a Schott filter (WG335) with a Hamamatsu photomultiplier (R2059) is monitored by a Camac ADC (Lecroy 2249W) connected to a personal microcomputer. The decay times are measured by means of a digital oscilloscope (Lecroy 9401) working in the sweeping mode.

Solution Experiments. Steady-state fluorescence measurements of 2-NetOH−camphor systems were performed with a Perkin-Elmer spectrofluorimeter in air equilibrated *n*-hexane solutions. The concentration of the 2-NetOH donor was $\sim 10^{-3}$ M, and aliquots (100 μL) of a 6.6×10^{-2} M solution of camphor in the same solvent were subsequently added. Since both the donor and acceptor absorb at the excitation wavelength (317 nm), the absorption spectra and molecular extinction coefficient were determined with a Cary spectrophotometer, ϵ(2-NetOH) = 155 M^{-1} cm^{-1} and ϵ(camphor) = 8.9 M^{-1} cm^{-1}, and the fluorescence intensity of the 2-NetOH compound has been corrected to take into account the inner filter effect due to the absorption of camphor and the dilution factor in the sample. A similar procedure was used for biacetyl and camphorquinone quenchers.

The fluorescence lifetimes of 2-NetOH solutions (deoxygenated by bubbling Argon) were determined with the same laser excitation as used in jet experiments (10 Hz, 8 ns width, dye laser beam set at 316 nm). The excitation was normal to the front surface of the cubic cell and the fluorescence was observed through the side face at 90° to the incident light through a low-resolution monochromator set at 340 nm. The decay times were measured as in the gas phase by means of the digital oscilloscope working in the sweeping mode. The fluorescence decay of 2-NetOH in air-saturated *n*-hexane solution has been measured independently using a single photon set up at the LURE with the synchrotron source of Superaco.

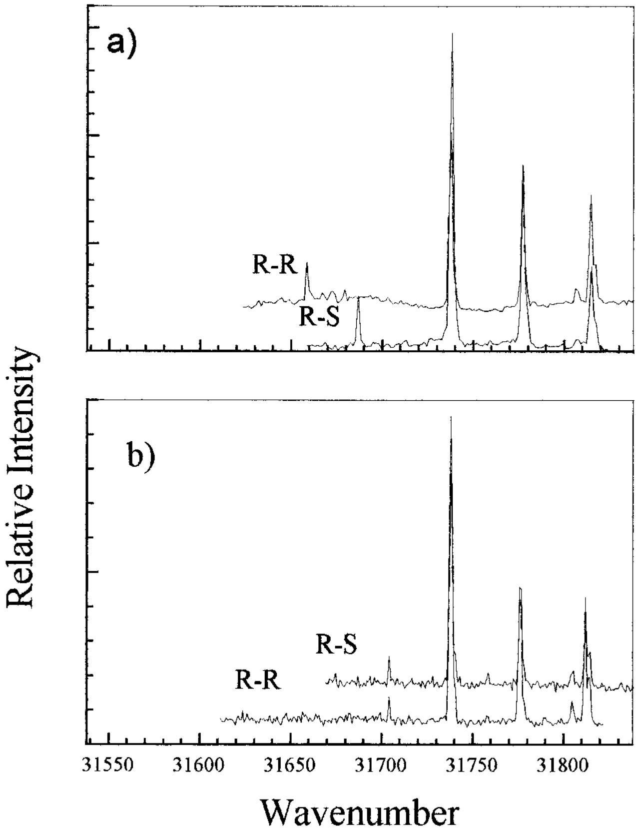


Figure 1. Low-energy part of the fluorescence excitation spectrum of the jet-cooled diastereoisomeric pairs formed by complexing *R*-2-NetOH with (a) *R*- and *S*-α-pinene and (b) *R*- and *S*-camphene.

Results

Jet Experiments. Figure 1 shows the fluorescence excitation spectra obtained by adding the chiral olefins (*R*- and *S*-α-pinene and camphene) to *R*- or *S*-2-NetOH in the supersonic jet. As described previously,[2,3] the three main bands at 31738, 31777, 31815 cm^{-1} belong to the bare 2-NetOH molecule and have been assigned to the 0−0 transition followed by two members of a low-frequency (39 cm^{-1}) progression characteristic of a torsion of the side chain of the chromophore. The new features appearing in the red of the 0−0 band characterize the formation of weakly bound complexes which manifest themselves by a shift of the S_0−S_1 0−0 transition of the naphthalene chromophore. As seen on the Figure 1a, the R−R and R−S complexes of 2-NetOH with α-pinene give rise to distinct features showing the nonequivalence of both diastereoisomers. The homochiral R−R (or S−S) complex exhibits a larger red shift of the electronic transition ($\Delta\nu = -79$ cm^{-1}) than the heterochiral R−S (or S−R) complex ($\Delta\nu = -54$ cm^{-1}). In contrast, no enantiodifferentiation is observed in the case of the complexes with camphene (Figure 1b) since only a single new band located at the same energy for the R−R or R−S association

TABLE 1: Shifts of the O−O Transitions of the NetOH Chromophore and Fluorescence Decay Times of the O° Level for Complexes of *R*-2-NetOH with Optically Active Terpenes[a]

complex		Δν (cm^{-1})	τ (ns)
α-pinene	RS	−54	44 ± 3
	RR	−79	34 ± 3
camphene	RS	−35	193 ± 5
	RR	−35	110 ± 5
borneol	RS	−191	
	RR	−162	
camphor	RS	−89	42 ± 3
	RR	−89	25 ± 3

[a] The origin of the bare 2-NetOH S_0−S_1 transition is at 31738 cm^{-1}, and its fluorescence decay τ = 45 ns.

is obtained to the red of the origin of the bare chromophore spectrum (Δν = −35 cm^{-1}).

In Table 1 are reported the fluorescence decay times of the complexes of 2-NetOH obtained by pumping their 0−0 transition. In each case, the homochiral and heterochiral pairs exhibit a different decay, showing that the excited state relaxation processes in the chromophore depend on which diastereoisomer is selected. Usually complexation is expected to induce a shortening of the lifetimes by increasing the density of bath states which promote the nonradiative pathways. However, complexation may also influence the intramolecular coupling scheme between the singlet and triplet manifolds of the chromophore thus modifying the rate of intersystem crossing.[6] This is particularly the case for naphthalene derivatives whose excited state lifetimes are known to be strongly sensitive to excess vibronic energy,[7,8] to the position of the substituent, and to complexation.[9,10] For the complexes involving α-pinene, a shortening is observed for the R−R (or S−S) pair while the R−S (or S−R) pair exhibits no change with respect to the bare chromophore (45 ns). The behavior of the complexes with camphene is more surprising since, although excited at the same energy, the R−S and R−R pairs exhibit different decay times which are longer than that of the bare molecule. The lengthening of the fluorescence lifetimes has already been observed previously for the complexes of 2-NetOH with aliphatic alcohols.[2,3] As discussed before, this effect can be attributed to the decrease of the intersystem crossing efficiency induced by the presence of the complexing agent particularly if ISC is promoted by accidental degeneracies between the S_1 and isoenergetic higher triplet states (T_n). Complexation may destroy or enhance these coincidences by shifting the energy level position and therefore affects considerably the rate of ISC. Comparison of sensitized phosphorescence and fluorescence excitation spectra brings a confirmation of this explanation in the case of complexes of 1-cyanonaphthalene,[9] and this effect may be common in complexes involving naphthalene derivatives.[10]

In Figure 2 are shown the fluorescence excitation spectra of mixtures of *R*-2-NetOH with *R*- and *S*-borneol and camphor. The origin bands corresponding to the R−R (Δν = −162 cm^{-1}) and R−S (Δν = −191 cm^{-1} and −177 cm^{-1}) 2-NetOH−borneol pairs are clearly differentiated while the camphor complexes display the same 0−0 band red shifted by 89 cm^{-1} from the bare molecule origin independently of the enantiomer. Both molecules present a similar bicyclic structure but contain specific functional groups, OH for borneol and C═O for camphor, which in contrast to the previous terpenes, may provide a localized point of interaction through the formation of a hydrogen bond with the OH group of the chromophore. However, despite the expected similitude of camphor and borneol complexes, their spectral properties differ significantly since no spectral discrimination can be achieved in the case of 2-NetOH−camphor diastereoisomers. The stereoselective interactions responsible for the enantiodifferentiation observed in van der Waals complexes between the 2-NetOH chromophore and alcohols have been previously attributed to the dispersive interactions which are enhanced in the case of folding of the attached solvent molecule over the naphthalene ring.[4] Although the lack of spectral discrimination for camphor complexes may be fortuitous, this result may also indicate that this system exhibits an extended geometry with a small overlap between the terpenic globular frame and the aromatic nucleus. Besides, since the enantiodifferentiation may be influenced by the location of the chiral center, it should be mentioned that in borneol, the asymmetric carbon is located next to the H bond between the two partners while the chirality of camphor is due to the carbon atoms belonging to the cycles which are more distant from the supposed C═O···HO link. The 2-NetOH−borneol spectra can also be compared with those observed with other secondary alcohols.[3] In this case also, the heterochiral complexes exhibit a larger red shift of the transition than the homochiral complexes. The presence of two bands of similar intensity for the R−S complex may be due to two different conformations of the borneol molecule, although this effect is not apparent for the R−R enantiomeric pair. In fact, it is known that the rotational orientation of the OH group of borneol gives rise to three possible conformations,[11] and it has been shown that only two of them (the gauche and the anti) are significantly populated at room temperature and thus expected to be cooled in the supersonic jet. The lack of low-frequency vibrational

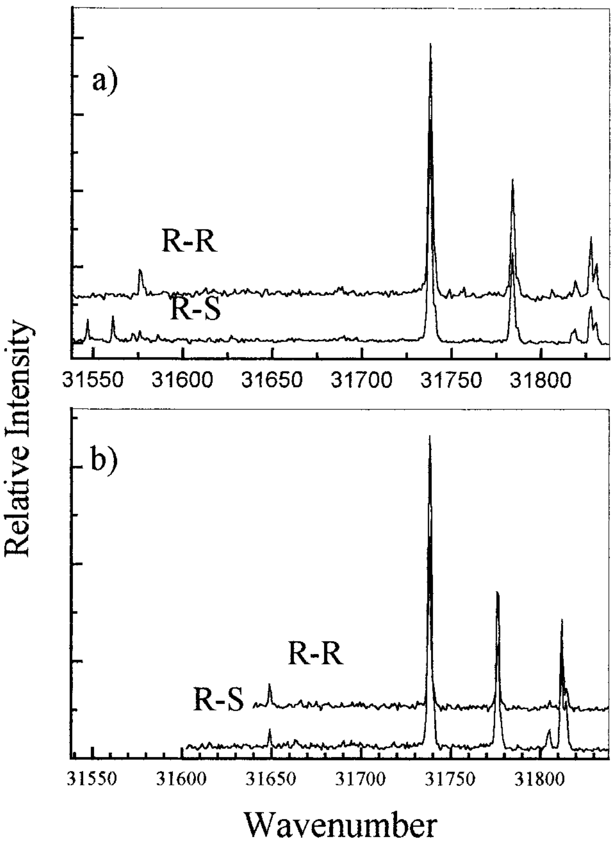


Figure 2. Low-energy part of the fluorescence excitation spectrum of the jet-cooled diastereoisomeric pairs formed by complexing *R*-2-NetOH with (a) *R*- and *S*-borneol and (b) *R*- and *S*-camphor.

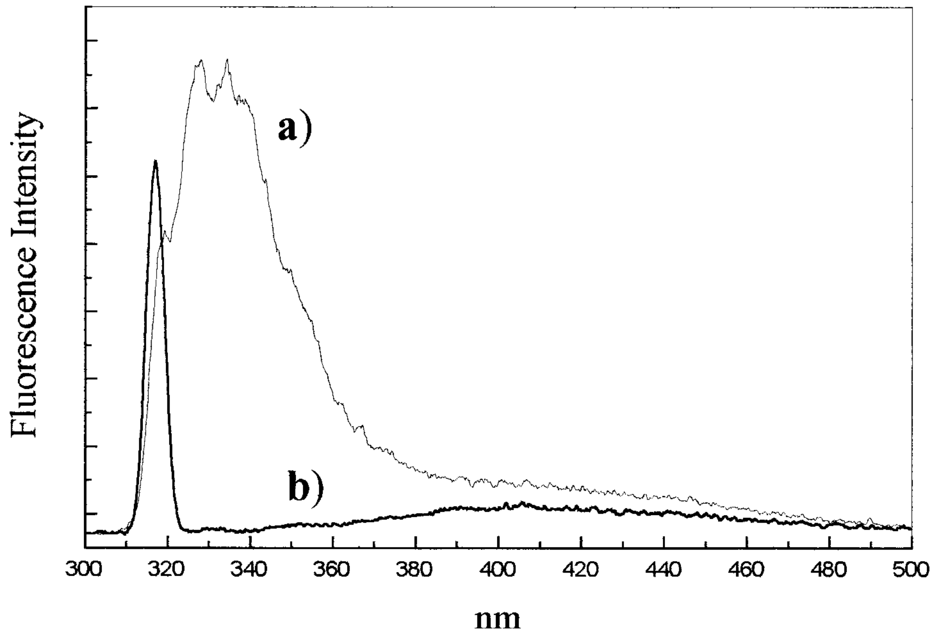


Figure 3. Fluorescence emission spectra of aerated *n*-hexane solutions of (a) *R*-2-NetOH (3.1×10^{-3} M) + *R*-camphor (1.12×10^{-2} M) and (b) pure *R*-camphor (1.12×10^{-2} M); $\lambda_{exc} = 317$ nm.

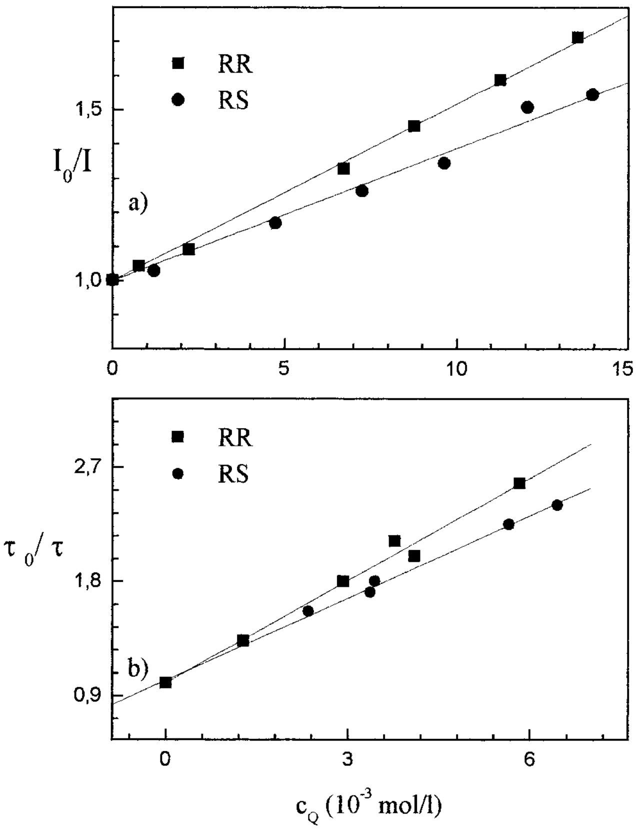


Figure 4. Stern–Volmer plots for fluorescence quenching of *R*-2-NetOH by *R*- and *S*-camphor in *n*-hexane: (a) steady-state intensity measurements in air-saturated solutions; (b) lifetime measurements in deaerated solutions.

structure in the spectra obtained with borneol relative to those obtained with the linear secondary alcohols may be related to the rigidity of the molecule and to its bulky structure with limited conformational freedom.

The fluorescence decays reported in Table 1 show that the excited R–R and R–S complexes with camphor, although excited at the same excitation energy, lead to different lifetimes; while the R–S is only slightly shorter than that of the bare molecule, the R–R complex exhibits a much shorter decay. As discussed above, this effect can be due to a very efficient intersytem crossing due to the occurrence of strong resonance in S_1–T_n interactions in this complex. However, in this case, besides the modification of intramolecular relaxation processes, intermolecular deactivation may also take place. Camphor as a ketone presents a very low absorption in the same energy range as 2-NetOH due to an n–π^* transition involving the carbonyl group, and the strong decrease in fluorescence lifetime of the R–R diastereoisomer may involve the singlet–singlet energy transfer between the two components of the pair according to

$$N^*{-}C \rightarrow N{-}C^*$$

(N stands for 2-NetOH and C for camphor)

Singlet–singlet energy transfer taking place from a donor to an acceptor associated in isolated van der Waals complexes has been already demonstrated in several systems[12,13] despite the difficulties inherent to the supersonic conditions (low concentration of complexes, absence of vibrational relaxation).

In the present case, such an assumption cannot be confirmed since camphor has too weak an emission to be detected in the conditions of the supersonic expansion. To have more information on the electronic energy transfer in these systems, the selective quenching of enantiomerically pure 2-NetOH chromophore by *R*- or *S*-camphor has been studied in solution.

Solution Experiments. Quenching of *R*- and *S*-2-NetOH fluorescence by *R*- and *S*-camphor in *n*-hexane solutions was studied both in steady-state conditions and by time-resolved measurements. The dispersed fluorescence spectra of aerated solutions of 2-NetOH in the presence of camphor excited at 317 nm (which corresponds to the 0–0 transition of the 2-NetOH molecule) show that the decrease of 2-NetOH fluorescence is complemented by the enhancement of the weak emission in the visible range due to the fluorescence of the camphor molecule (Figure 3). This result demonstrates that the observed quenching process involves a singlet–singlet energy transfer from the naphthalene derivative as the donor to the camphor as the acceptor. The Stern–Volmer plots for the

TABLE 2: Fluorescence Quenching Constants of *R*-2-NetOH by Chiral Quenchers

solvent	donor	acceptor	K_{sv} (M^{-1})	$k_Q{}^a$ (10^9 M^{-1} s^{-1})	$k_Q{}^b$ (10^9 M^{-1} s^{-1})
n-hexane	*R*-NetOH	*R*-camphor	51 ± 3	7.3	7.36
	R-NetOH	*S*-camphor	39 ± 3	5.6	6.0
	R-NetOH	*R*-camphorquinone	187 ± 10	27.1	
	R-NetOH	*S*-camphorquinone	193 ± 10	27.8	
	R-NetOH	biacetyl	190 ± 10	27.5	

[a] Deduced from $K_{sv} = k_Q\tau_0$ with $\tau_0 = 6.9$ ns for 2-NetOH in *n*-hexane at 20 °C. [b] From fluorescence decay time measurements.

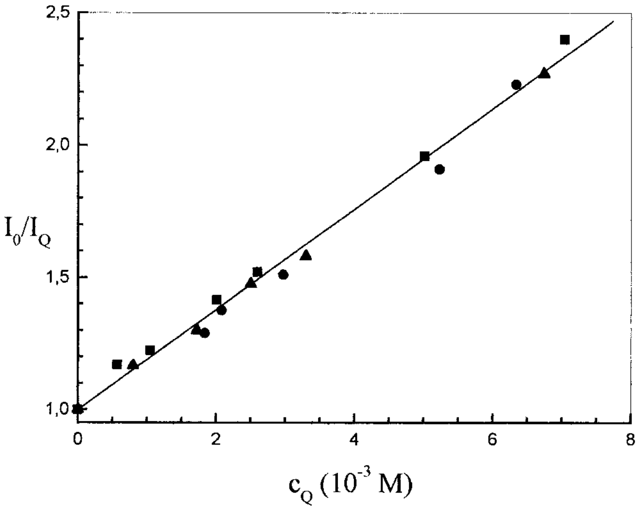


Figure 5. Stern−Volmer plots for quenching of *R*-2-NetOH with biacetyl (●) and *R*-(▲) and *S*-camphorquinone (■) from steady-state intensity measurements.

quenching of the relative donor fluorescence quantum yields I_0/I_Q in the absence and in the presence of quencher as a function of the camphor concentration (c_Q) in aerated solutions were found to be linear for concentrations between 10^{-3} and 2 × 10^{-2}M (Figure 4a) in agreement with the relation

$$I_0/I_Q = 1 + K_{SV}[c_Q] \text{ with } K_{SV} = k_Q\tau_0$$

and Stern−Volmer coefficients K_{SV} deduced from the slopes are reported in Table 2. The quenching rate constants k_Q for the different enantiomeric mixtures were obtained from the relation $K_{SV} = k_Q\tau_0$, where the lifetime of NetOH in aerated *n*-hexane solutions $\tau_0 = 6.9$ ns (Table 2). These data are in good agreement with the rate constants deduced from fluorescence lifetimes measured in deaerated *n*-hexane solutions as shown on Figure 4b and Table 2. For the sake of comparison, steady-state quenching of the *R*- and *S*-2-NetOH chromophores has also been determined with other ketones: biacetyl and *R*- and *S*-camphorquinone (Figure 5). The electronic energy transfer is conclusively established in these systems by the concomitant observation of the diketone fluorescence and the K_{SV} coefficients and k_Q rate constants are reported on Table 2. Strong differences can be seen in the fluorescence quenching of 2-NetOH by camphor and biacetyl and camphorquinone from the comparison of the data of Table 2.

(i) The quenching rate constants k_Q are smaller by a factor of ∼4 for camphor than for biacetyl and camphorquinone.

(ii) In the case of camphor as the acceptor, a chiral discrimination is obtained, while no dependence on the chiralty is observed in the case of camphorquinone.

Quenching Rate Constants. In the 2-NetOH−biacetyl or camphorquinone systems, k_Q is very close to the diffusion-controlled rate constant given by the Smoluchowski equation,

$$k_{dif} = 4\pi N\sigma D/1000[1 + \sigma/(D\tau_0)^{1/2}] \tag{1}$$

where σ is the sum of the collision radii of the donor and the acceptor, D is the sum of their diffusion coefficients derived from the Stokes Einstein relation for low viscosity ($D = 66.9$ 10^{-6} cm^2 s^{-1} for *n*-hexane at 20 °C), and τ_0 is the lifetime of the excited donor.

With $\sigma = 5.5$ Å, k_{dif} can be estimated to 2.9 10^{10} M $^{-1}$ s^{-1} while the Debye limit $k_{dif} = 8RT/3000\eta$, where η is the viscosity of the medium, gives $k_{dif} = 2.1 \times 10^{10}$ M^{-1} s^{-1} for *n*-hexane at 20 °C.

Diffusion-limited energy transfer is characteristic of donor−acceptor systems for which the oscillator strengths of the associated transitions are low and indicates that the energy transfer proceeds at short distances through an electron exchange in a collision complex according to the Dexter mechanism,[14] as in the model case of naphthalene−biacetyl system.[15] The energy transfer step given by

$$k_{et} = 2\pi/hZ^2J = 2\pi/hKJe^{-2R/L} \tag{2}$$

(where J is the spectral overlap integral and Z^2 the exchange term for the electrons involved in the transition, which can be reduced to $Ke^{-2R/L}$, with K a constant, R the distance between donor and acceptor, and L the Bohr radius for the excited state donor and ground state acceptor orbitals taken as hydrogenoid orbitals) is fast relative to the rate of formation of the encounter complex which is then the rate-determining step.

Since the energy transfer to camphor involves the same donor $\pi-\pi^*$ state and a similar weakly allowed $n\pi^*$ acceptor state as previously, the short-range mechanism is also expected to operate in this case. The lower rate constant obtained with camphor should thus be related to the exothermicity of the energy transfer process; while in the case of diketones, the energy gap between the donor and acceptor energy levels is respectively of about 9100 cm^{-1} (26 kcal/mol) for biacetyl and 10800 cm^{-1} (30.8 kcal/mol) for camphorquinone, the singlet 2-NetOH donor and camphor acceptor states are almost isoenergetic. The exact energy gap is difficult to deduce from absorption spectra in solution since the 0−0 transition of camphor is not clearly seen. Furthermore, the fact that the fluorescence of camphor exhibits a rather large Stokes shift indicates a significant modification of excited state geometry for the ketone and a low Franck−Condon factor for the 0−0 transition. Nevertheless, for energy differences less than 3 kcal/mol, as is the case in the 2-NetOH camphor system, besides back transfer which leads to a decrease of the quenching efficiency, the rate of forward reaction should also decrease for energetic reasons and becomes the rate-determining step.

Chiral Discrimination. The rate of quenching obtained with camphor is found to depend on the chirality, and the homochiral systems exhibits a larger rate constant than the heterochiral ones.

The chiral discrimination factor in enantiomeric pairs k_Q(R−R or S−S)/k_Q(R−S or S−R) = 1.23, although weak, is larger than the experimental error estimated as 5%. Since a close contact pair is needed to reach enantioselectivity, this result corroborates the short-range mechanism for the energy transfer from the chiral NetOH to the chiral camphor. Furthermore, the preference for homochiral over heterochiral quenching reproduces to a lesser extent the trend obtained in the isolated pairs in the gas phase.

In contrast to the quenching by camphor, no chiral discrimination is obtained in the case of camphorquinone. This result can be understood since for diffusion-controlled energy transfer, the process is expected to be independent of specific donor acceptor interactions. For example, no steric effects have been found in the exothermic energy transfer between differently encumbered ketones and diketones which has been shown to be limited by diffusion.[16]

Conversely, when the process is not controlled anymore by the diffusion that determines the formation of the contact pair but by the probability of reaction within the collision complex as it is observed for the quenching by camphor, the stereochemical conformation of the enantiomeric pairs may thus influence this probability by acting on the electron exchange integral according to the Dexter theory. Similar enantioselective slow energy transfer has been reported between asymmetrical metal complexes using chirooptical time-resolved experiments.[17] The results have been interpreted in terms of the electronic exchange mechanism where both structural factors related to the intermolecular distance of approach of the donor and the acceptor and pure stereoelectronic interactions involving the relative orientation of molecular orbitals at a fixed distance contribute to the quenching kinetics.

It should be mentioned that a number of other studies have been devoted to evidence enantioselectivities in photoinduced bimolecular reactions such as electron transfer, exciplex formation,[18,19] and proton transfer.[20] In all these experiments, the mechanism for the observed quenching of fluorescence involves the formation of a transient close contact pair where geometrical factors are determinant to achieve significant chiral differentiation.

It is interesting to compare the quenching rate constants measured in solution with that obtained in the gas phase for the isolated complexes frozen in a given geometry. While the lifetime for the donor excited state gives a limiting value for the transfer rate in the isolated homochiral pair of the order of the 2×10^7 M^{-1} s^{-1}, it is 2 orders of magnitude higher in solution. This strong difference may hold only for the 0−0 level of the complex since the comparison of REMPI and fluorescence excitation spectra in jet-cooled conditions[5] indicates that the lifetime of the complexes should decrease rapidly above the origin as no fluorescence is observed above this band while the REMPI spectrum exhibits other features at higher energy. Thermodynamical factors may explain the larger rate obtained in solution; in quasithermoneutral systems, the Boltzmann distribution of rovibrational levels in the ground state should facilitate the reaction. Furthermore, it has to be noted that the Dexter formula (2) is valid for thermalized systems in solution and cannot be applied directly to the supersonic jet situation;[21] because of the single vibronic excitation and the absence of vibrational relaxation, the resonant emission of the donor and the structured vibrational pattern of the acceptor absorption, the coupling between discrete levels has to be considered in the electron exchange model. The larger chiral discrimination obtained for isolated pairs may then be attributed to differences in the overlap of the molecular orbitals involved in the electron exchange process[22] for the well-defined geometry of the two partners in the diastereoisomers.

Conclusion

The influence of chirality on the photophysical properties of the complexes of the optically active 2-NetOH chromophore with globular terpenic molecules has been examined in the isolated diastereoisomeric pairs formed in a supersonic expansion by studying both the shift of the S_0−S_1transition and the fluorescence decay of the excited state. The results have shown that even when no spectral discrimination is observed, chirality-dependent effects can be observed in the dynamics of the excited state. The enantioselective quenching of the 2-NetOH S_1 state by camphor observed in the jet-cooled complexes has also been observed in solution and has been shown to be due to singlet−singlet electronic energy transfer. In contrast to the exothermic transfer process obtained with biacetyl and both enantiomers of camphorquinone, the rate constant for quenching by camphor is smaller than would be expected for diffusion-limited kinetics because of the quasi-isoenergetic situation of the donor and acceptor levels. The chiral discrimination observed in the electronic energy transfer in this system gives evidence for the influence of the relative orientational geometry of the partners in the electron exchange integral involved at short distance according to the model of Dexter.

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