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1971–1976 – Profiting from a New Beginning in Geneva

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Abstract: A few projects of organic photochemistry, which have been investigated in Geneva in 1971–76, are reviewed summarily. They include excited state-selective processes from the n,π^* and π,π^* triplets and selectively occurring $\pi \rightarrow \pi^*$ induced reactions of α,β-unsaturated cyclic ketones, oxadi-π-methane rearrangements and 1,3-acetyl shifts of β,γ-unsaturated methyl ketones, and di-π-methane rearrangements of benzoylnaphthobarrelene compounds. Furthermore, intramolecular triplet energy transfer dependence on rigid donor–acceptor *syn-anti* topologies between indanone and naphthalene moieties most likely reflects competition between radiationless energy dissipation by through-space aromatic π interaction (amounting to intramolecular exciplex action) and through-σ-bond exchange transfer. Finally, electronically integrating actinometry and time-resolved IR spectroscopy of excited states and reaction intermediates are mentioned.

Keywords: Electronically integrating actinometer · Excited state-selective photoreactions · Intramolecular energy transfer dependence on donor–acceptor topology · Time-resolved IR spectroscopy · α,β-and β,γ-Unsaturated ketones

During the mid-20th century chemistry departments – like other university branches – had lived through decades of growth. Able young scientists, hesitant to apply for openings in an equally fast growing chemical industry, had fair chances to be offered a university position, and indeed many were fortunate enough to have a choice between more than one. I was one of these. In 1971 I decided accordingly, at the age of 40, that I should look for a change and move from the Organic Chemistry Laboratory of ETH Zürich. I had spent all my scientific training and research years at ETH, apart from a postdoctoral year and a few visiting professorships abroad. At that point, I was (and still am) grateful to look back on altogether 16 years of association with Professor *Oskar Jeger*. When a postdoc at Brandeis University, Waltham/Boston, I had received out of the blue an offer by Jeger for an assistant position which included the attractive burden to supervise his entire group. This was too good to turn down. It made me pack up my belongings, in fall 1958, and forget about my US immigration status.

Jeger's expectation, distinctly in the air although hardly ever spoken, was that in due course I should recruit a group of my own in parallel to my involvement with some twenty of Jeger's students. Of course this also meant that I increasingly occupied lab space of Jeger's for my own purpose, and that at the beginning I drew some of his financial support before I received any own funding. Most important, however, was Jeger's regular advice and encouragement. By 1970 I felt ready to tackle any new challenge, wherever, within the frame of an academic career.

And this was to be at the *Département de Chimie Organique* of the University of Geneva. In fall 1971 chemistry had moved into a brand new building, *Sciences II*, located on the quiet *quai Ernest-Ansermet* overlooking the river *l'Arve*, a pieceful setting a few walking minutes from downtown Geneva.

By 1971 the organic chemistry department had been downscaled to a critical size: one professor, *Charles Jefford*, one assistant, *Paul Müller*, and *Ulrich Burger*, a postdoc from Munich who had just joined Jefford's group. Charles had gained his chemistry degrees in Oxford, served time as a professor in Philadelphia and came to Geneva in 1969 *via* another professorship at the University of Marseilles. Although encouraged by Dean and Rector, and supported by a few well-meaning colleagues from the other chemistry departments – but stiffly opposed by others – his initial enthusiasm to mould the existing remains of an organic chemistry laboratory into a thriving and competitive department had considerably dwindled by the time of my arrival. However, for a nucleus of four – Jefford, Müller, Burger and myself – things soon looked brighter. Financial support by the *Nationalfonds* and the chemical industry (Ciba-Geigy AG, Firmenich & Cie) afforded motivation and substantial supplementation of sophisticated departmental state-of-the-art instrumentation. Burger proved to be an able provider of service with the more demanding spectroscopic techniques. A trio of doctoral students, *Walter Amrein*, *Hans-Ulrich Gonzenbach* and *Jean Gloor*, who had moved with me from Zurich, preferring to continue with their doctoral work in Geneva, eagerly started to supplement the empty laboratories. My group soon was joined by several additional students from Geneva and Zurich – *Inga-Mai Tegma-Larsson*, *Jean Gauthier*, *Jean-Pierre Grosclaude*, *Raul Mariaca*, *Frédéric Nobs*, *Jean-Claude Perlberger* and *Beat Winter*, and by *Christopher O. Bender*, on sabbatical leave from the University of Lethbridge, Alberta, and three postdoctoral fellows, *Uwe Klinsmann* and *Paul Margaretha* from Germany, and eventually *Martin Demuth* from Zurich.

The following years were characterized by pioneering enthusiasm. Everybody seemed to feel that he had a mission, toward building up a department compara-

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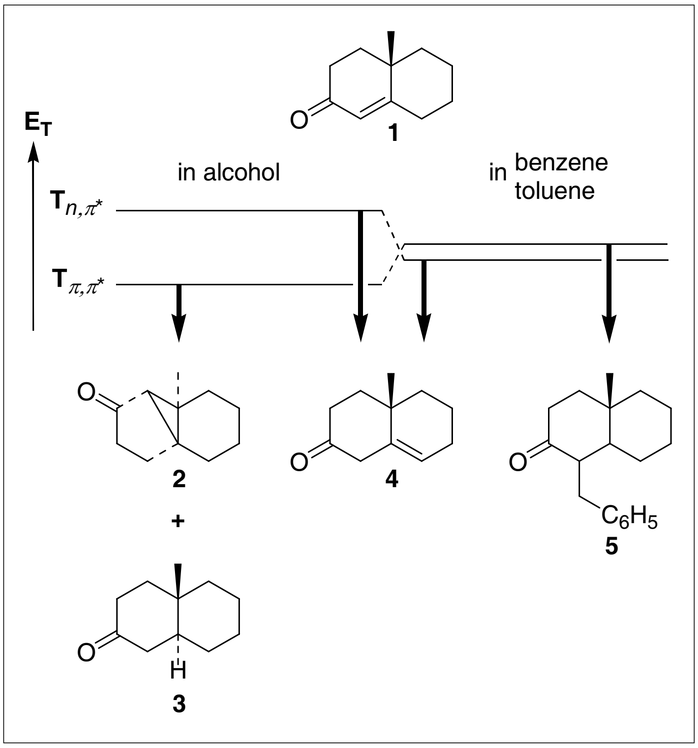
ble in terms of teaching quality and significance of scientific achievement to other schools within our country and beyond. It was great fun, for graduates, assistants and professors alike, and well worthwhile.

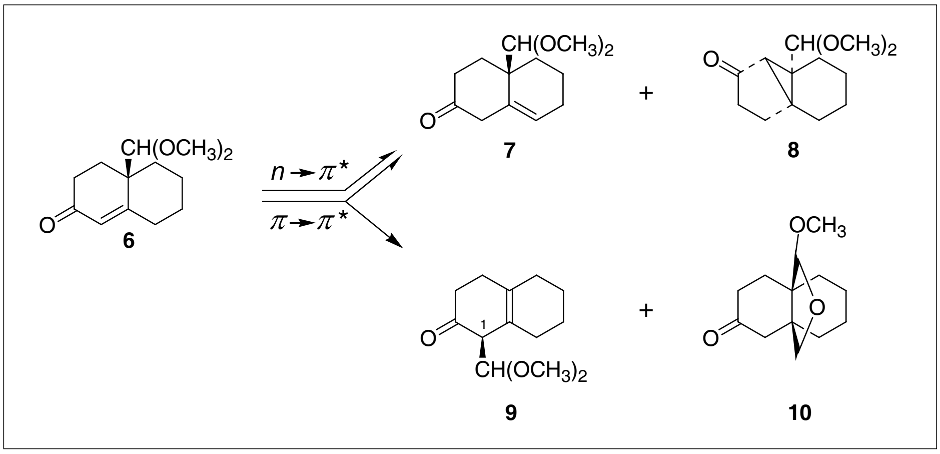
In 1974 we could welcome a third professor of organic chemistry, *Wolfgang Oppolzer*, a very gifted synthetic organic chemist. Wolfgang, a doctoral student of Professor *Vlado Prelog* at ETH, had embarked on a career in pharmaceutical research at Sandoz in Basel when he learned of our interest to offer him an opening, which he accepted enthusiastically. He proved to be a very important complement to the departmental staff, an inspiring teacher and a brilliant scientist reinforcing the international standing of our department.

Once installed in Geneva, the main research of my group continued to address mechanistic organic photochemistry. Several topics will be highlighted in the following. Most have in common that photoreactions do not necessarily occur from the first(lowest)-lying excited state of a given spin manifold. Rather, a reaction may compete with demotion to the first excited state, *e.g.* internal conversion, $S_2 \rightarrow S_1$, and intersystem crossing, $S_1 \rightarrow T_1$, are not always the processes to occur prior to chemical reaction. Some of these investigations were followed up after their initiation at ETH,[1–3] and most were eventually concluded after my move from Geneva to the *Max-Planck-Institut für Strahlenchemie* in Mülheim an der Ruhr in fall 1976.[4–8]

One focus was on the excited state-selective reactions which we had come upon when still at ETH. Thus, conjugated cyclohexenones in solution undergo unique transformations, often in good chemical yields, which have caught wide attention in view of intriguing mechanistic questions involved.[9] For example, diverse triplet photoreactions of an enone are subject to distinct solvent effects reflecting specifically differential reactivities of the primary processes of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states, as exemplified for octalone **1** (Scheme 1).[2]



Scheme 1. Excited state-selective reactions from the *n*,π* and π,π* triplets of 10-methyl-$\Delta^{1,9}$-octalone-(2) (**1**).[10]



Scheme 2. Excited state-specific reactions from the *n*,π* (→ **7**) and π,π* triplets (→ **8**) and from the π,π* singlet (→ **9** + **10**) of 10-dimethoxymethyl-$\Delta^{1,9}$-octalone-(2) (**6**).[10]

The double bond shift to **4** was shown to occur by abstraction of an allylic hydrogen from ground state **1** by the oxygen of a $^3(n,\pi^*)$ enone. Alternatively, the primary reaction of the formation of **5** was attributed to hydrogen abstraction from toluene by the β-carbon of $^3(\pi,\pi^*)$-**1**, a process ascribed also to the double bond reduction in isopropanol to **3**. The solvent effects on the product distribution comply with the assigned nature of the reactive triplets.

In continuation of such studies in Geneva the validity of the interpretation of these solvent effects in terms of specific $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ state reactivities was confirmed in related systems. As a spin-off of the probing into the electronic specificity of excited-state reactions of enone analogs of **1**, however, other types of photoreactions were encountered as well. Thus, specific product formation from the higher lying $^1(\pi,\pi^*)$ state, S_2, was observed upon selective irradiation into the first π → π* absorption band with wavelength of 254 nm. The dimethoxymethyl analog of **1**, compound **6**, afforded the *n*,π* (**7**) and π,π* triplet products (**8**), and the π,π* singlet products **9** and **10** (Scheme 2). [11,12]

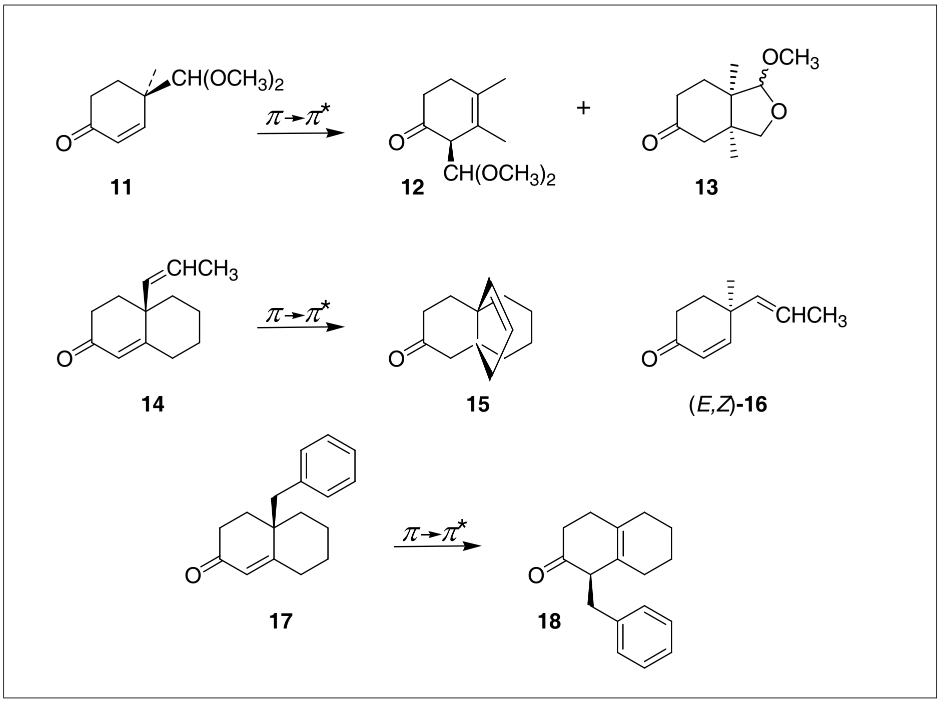
S_2 Reactions of types **6** → **9** + **10** are not restricted to the octalone ring system and to dialkoxymethyl substituents. Thus, analogous findings were encountered also with monocyclic enones such as **11**[11b] and with the 1-propenyl, **14** (cyclization to **15** only),[13,14] and benzyl octalones, **17** → **18** (Scheme 3).[15] Configurational and isotope-labelling (crossing) experiments showed that the allylic 1,3-shifts such as **6** → **9** occur predominantly *via* a tight radical pair without intermolecular scrambling,[16] and that cyclizations of type **6** → **10** involve intramolecular methoxyl hydrogen abstraction by the enone α-carbon in the primary step.[3,11a,b]

When still at ETH, selective product formations had also been found upon direct and triplet-sensitized excitation of aliphatic β,γ-unsaturated ketones: *e.g.* enone **19**, upon direct *n* → π* excitation, undergoes a sigmatropic 1,3-acetyl shift, (*R*)-**19** → (*S*)-**19**, as the major unimolecular reaction in the excited singlet state, and upon sensitization a (thermally reversible) 1,2-acetyl shift, with cyclopropane ring closure (an oxadi-π-methane rearrangement) to *endo*- and *exo*-**20** as the predominant triplet state reaction (Scheme 4).[17,18] Alternatively, an oxadi-π-methane rearrangement analogous to **19** → **20** is not competitive with the more efficient recombination/disproportionation and dissociation in geminate singlet and triplet radical pairs of aroyl analogs such as summarized in Scheme 5 for **21** and **22**.[19] In Geneva,[20] and subsequently in Mülheim,[8] the 1,3-acetyl shift and oxadi-π-methane rearrangement of compounds of type **19** were analyzed eventually in great detail.

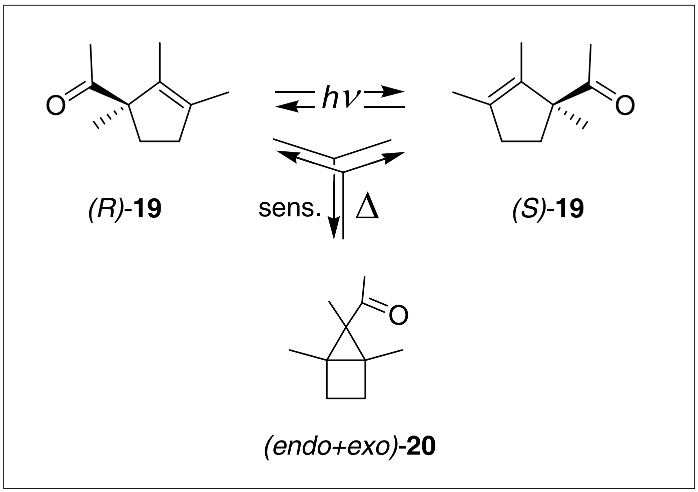
A considerably more complex excited-state reaction diagram was encountered with the photorearrangement of the benzoylnaphthobarrelene-like compounds **23** and **25** (Scheme 6).[4,5] Both systems rearrange in di-π-methane-type processes, *viz.* **23** → **24a**–**c** and **25** → **26a** + **b**. While the three isotopomeric products **24a**–**c** are not interconvertible photochemically, a thermal equilibrium among **23** and **24a**–**c** is attained at 493 K. The primary photoreaction of **23** directly occurs from the $S_1(n,\pi^*)$ and $T_2(n,\pi^*)$ states, and it proceeds from $T_1(\pi,\pi^*)$ and $S_2(\pi,\pi^*)$ either directly or *via* T_2 (Fig. 1).

The subsequent rearrangement steps of **23** to **24a**–**c** evolve along three reaction paths from the two primary photochemical processes of naphthyl-vinyl and vinyl-vinyl bonding in β-position to the carbonyl group. Two ground-state triplet diradicals have been shown, by ESR, IR, fluorescence and fluorescence excitation, and by laser flash photolysis, to intervene consecutively.[4,5b] It was of interest to note that **23** and **24** thermally interconvert in the dark, which constitutes a ground-state counterpart of the di-π-methane-type photorearrangement, and that the sequence of the photoreaction **23** → **24** (with a high quantum yield of $\Phi = 1.0$ at 298 K), followed by a smooth electrophile-catalyzed reversal in the dark amounts to a chemical light energy storage cycle conductible without loss of energy.[21]

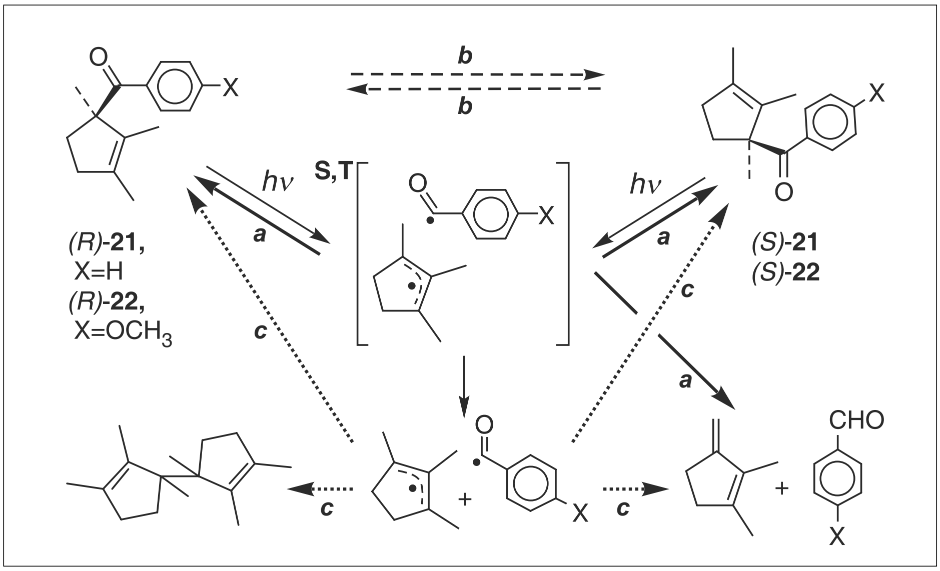
Another study of photoprocesses carried out in Geneva that I should like to mention here relates to the intramolecular energy transfer in conformationally rigid molecules with stereoisomerically oriented donor and acceptor groups (Fig. 2). The ketone donor consistently increases the naphthalene phosphorescence quantum yield more strongly in the *exo* configuration (**29**) than in the corresponding *endo* isomer (**27**)



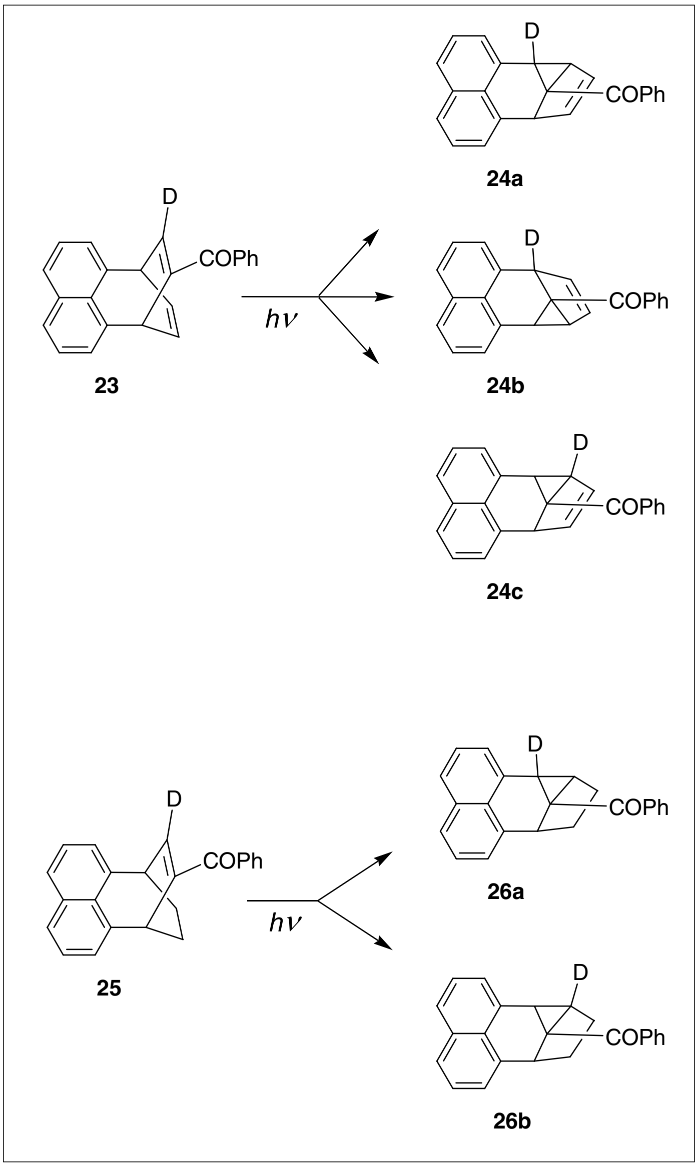
Scheme 3. Excited state-specific reactions from the π,π* singlet states of 4-dimethoxymethyl-4-methyl-2-cyclohexenone (**11**) (→ **12** + **13**), 10-(*E,Z*-1-propenyl)-$\Delta^{1,9}$-octalone-(2) (**14**) (→ **15**), and 10-benzyl-$\Delta^{1,9}$-octalone-(2) (**17**) (→ **18**).[10]



Scheme 4. Direct irradiation and triplet-sensitized excitation of 3-acetyl-1,2,3-trimethlcyclopent-1-ene (**19**).[10]



Scheme 5. Photochemical α-cleavage of β,γ-unsaturated aryl ketones **21** and **22**.[10] *a* = Geminate radical pair reactions; *b* = reaction paths bypassing polarizable radical intermediates; *c* = free radical reactions.



Scheme 6. Di-π-methane photorearrangement of the benzoyl-naphthobarrelene-like compound **23** (→ **24a–c**) and of the dihydro analog **25** (→ **26a** + **b**).[10]

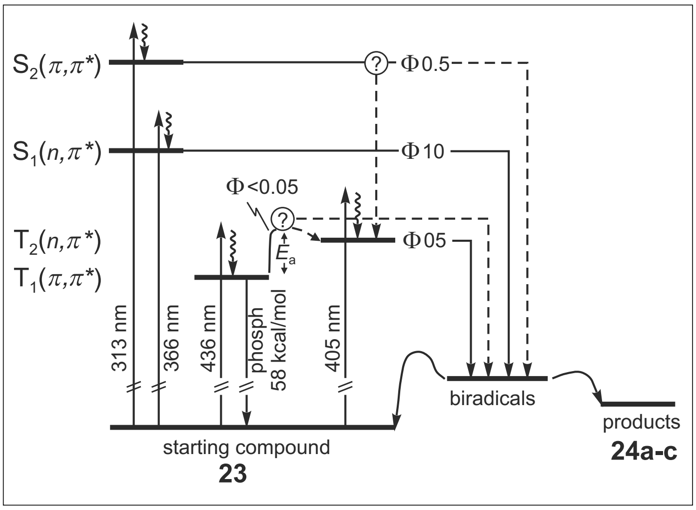


Fig. 1. State and reaction diagram for the photorearrangement of **23** → **24a–c**. Branching broken arrows (- - -) designate processes not discriminated by experiment

[factor $\chi = \Phi_p$(ketone/$n \rightarrow \pi^*$ excitation) / Φ_p(hydrocarbon/^1L_b excitation) varies from 3 for **29/30** to 5 for **27/28**], *viz.* the triplet energy transfer is more efficient in the *exo* than in the *endo* configuration.[22] In both configurations an efficient through-σ-bond exchange transfer mechanism evidently is operative, and in the *endo* configuration an additional mechanism, *e.g.* one based on through-space interaction, competes with the population of the triplet naphthalene state. A weak intramolecular exciplex, T(DA) in Fig. 3, offers a mechanistically plausible route for additional radiationless energy dissipation by through-space interaction in the *endo* configuration.

Two instrumental developments – an electronically integrating actinometer for quantum yield determinations of photoreactions in solution and an IR flash photolytic set-up – were initiated in our Geneva group. The actinometer was ready for routine use in late 1973.[23] It was designed to provide continuous reading, under daylight conditions, of the light flux absorbed in the photochemical sample solution. The detector system monitors the flux difference in front and behind the sample cell. The differential flux measurement is independent of incident wavelength and proportional to the light quanta absorbed. Eventually, an advanced instrument (‘Quantacount’) of this kind became commercially available.[24] Technically a greater challenge was the construction of a flash photolysis apparatus with IR detection, the initial development phase of which was started in Geneva with financial backing by CIBA-Geigy.[25] The first finalized instrument was on the bench in Mülheim shortly after 1980.[6] At the best, time-resolved IR (TRIR) detection allows in solution at room temperature the study of excited states, intermediates, and their transformation into stable products with a spectral resolution that often is significantly better than UV-vis absorption spectroscopy. TRIR was the first to bridge the gap to spectral data obtained at low temperatures in rigid matrices. It provides information which has previously been inaccessible, such as detailed structural information, and kinetic data in cases where the UV-visible absorptions of the species of interest overlap. Moreover, excited-state TRIR, at a time resolution of ≥50 ns, had become feasible for many organic compounds; *e.g.* the differentiation between lowest-lying *n*,π* and π,π* triplets of aryl ketones.[26]

After five enjoyable years of teaching and research in Geneva, I was confronted with the attractive offer to become a director at the *Max-Planck-Institut für Strahlenchemie*. My spontaneous reaction was hesitant, however. It was difficult to decide against Geneva. Nevertheless, I chose to move north, with good memories of five years fruitfully spent, and with a bag full of exciting research projects to be taken to Mülheim and to be finished. The completion of these projects, in some instances benefiting from superior latest equipment and expertise,[4b,5a,b,6a,7,8,26] contributed meaningfully to a fresh start of research in a new surrounding, and it helped to bridge time in the initial phase of entering photobiology, a new field for all participants concerned.[27]

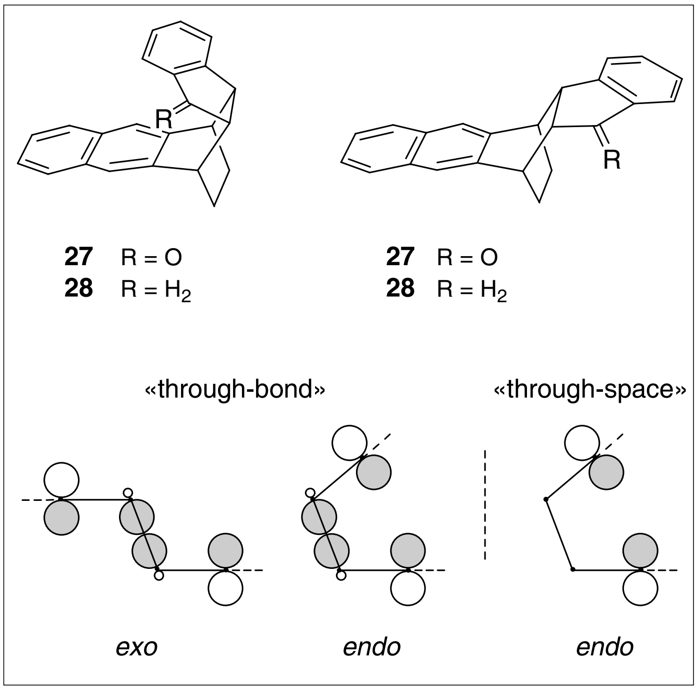


Fig. 2. Through-σ-bond (in compounds **27** und **29**) and through-space interactions (in **27**) between indanone and naphthalene chromophores.[10]

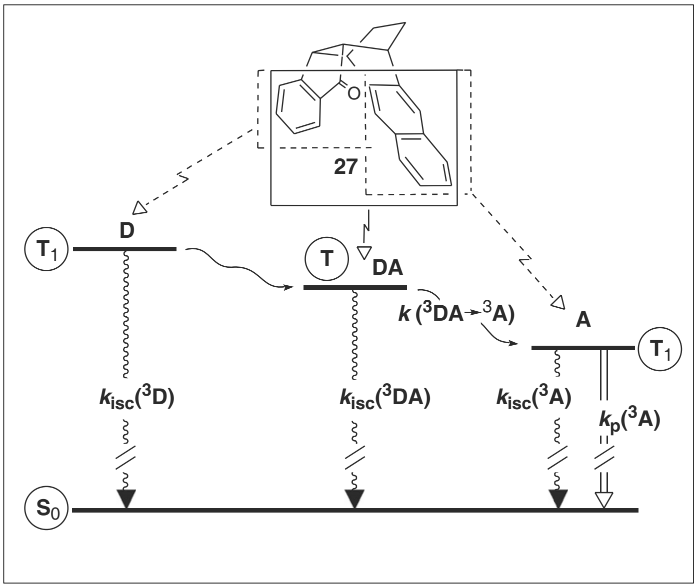


Fig. 3. Intervention of a weak intramolecular exciplex in the *endo* triplet energy transfer of **27**.[10]

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