[4] *L. Friedman & F. M. Logullo*, J. Amer. chem. Soc. *85*, 1549 (1963); J. org. Chemistry *34*, 3089 (1969).
[5] *D. Seebach*, Angew. Chem., Int. Ed. Engl. *8*, 639 (1969); Synthesis *1*, 17 (1969).
[6] *E. J. Corey & B. W. Erickson*, J. org. Chemistry *36*, 3553 (1971).
[7] *P. S. Wharton & D. H. Bohlen*, J. org. Chemistry *26*, 3615 (1961).
[8] *E. A. Braude & J. A. Coles*, J. chem. Soc. *1952*, 1430; *E. A. Braude & W. F. Forbes*, ibid. *1953*, 2208.
[9] *H. O. House, V. Paragamian, R. S. Ro & D. J. Wluka*, J. Amer. chem. Soc. *82*, 1457 (1960); *H. O. House, T. M. Bare & W. E. Hanners*, J. org. Chemistry *34*, 2209 (1969).
[10] *A. B. Smith, III & W. C. Agosta*, J. Amer. chem. Soc. *95*, 1961 (1973).
[11] *W. Amrein & K. Schaffner*, unpublished results.
[12] *H. E. Simmons*, J. Amer. chem. Soc. *83*, 1657 (1961).
[13] *J. Meinwald, G. E. Samuelson & M. Ikeda*, J. Amer. chem. Soc. *92*, 7604 (1970).
[14] *W. Hartmann & H.-G. Heine*, Angew. Chem. *83*, 291 (1971); *J. Shields, D. Gavrilovic, J. Kopecký, W. Hartmann & H.-G. Heine*, J. org. Chemistry *39*, 515 (1974); *cf.* also *I. Murata & K. Nakasuji*, Tetrahedron Letters *1973*, 47; *R. M. Pagni & C. R. Watson*, ibid. 59.
[15] *V. Boekelheide & G. K. Vick*, J. Amer. chem. Soc. *78*, 653 (1956).
[16] *C. S. Marvel & W. C. Hinman*, J. Amer. chem. Soc. *76*, 5435 (1954).
[17] *T. Naito, S. Nakagawa & J. Okumura*, U.S. Pat. 3 360 527; *cf.* Chem. Abstr. *69*, 36 117g (1968).
[18] *A. Dunand & R. Gerdil*, Helv. *58*, in preparation (1975).
[19] *J. C. Collins, W. W. Hess & F. J. Frank*, Tetrahedron Letters *1968*, 3363.
[20] Cf. *A. J. Birch & K. A. M. Walker*, J. chem. Soc. C *1966*, 1894; Tetrahedron Letters *1967*, 1935; *M. Brown & L. W. Piszkiewicz*, J. org. Chemistry *32*, 2013 (1967).

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48. A Study of Intramolecular Energy Transfer in Conformationally Rigid Molecules with Stereoisomerically Oriented Donor and Acceptor Groups

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(3. XII. 74)

Summary. The indanono naphthaleno compounds **1**, **3**, **5** and **7** exhibit, on both irradiation in the ^1L_b band (315 nm) and the $n \rightarrow \pi^*$ transition (> 340 nm) in EPA at 77°K, neither fluorescence from naphthalene nor phosphorescence from indanone, but exclusively phosphorescence from naphthalene, and quenching in liquid solution with 1,3-pentadiene results in triplet energy transfer from the naphthaleno group only. The naphthalene phosphorescence exhibited by the ketones (**1**, **3**, **5**, **7**) has an enhanced quantum efficiency with respect to that on direct excitation of the corresponding hydrocarbons (**2**, **4**, **6**, **8**), and more strongly in the *exo* than in the *endo* orientation. In order to account for the energy wasting in the intramolecular triplet energy transfer in the *endo* compounds, a transfer route *via* a weak triplet donor-acceptor exciplex, specific to through-space interaction in the *endo* configuration (providing for additional radiationless T → S energy dissipation through vibrational coupling), competing with an efficient through-σ-bond exchange transfer mechanism operative in both configurations is proposed.

During the last 13 years numerous studies of the transfer of electronic energy between non-conjugated donor and acceptor chromophores within the same molecule have been published. The interest in this field is motivated by both photophysical

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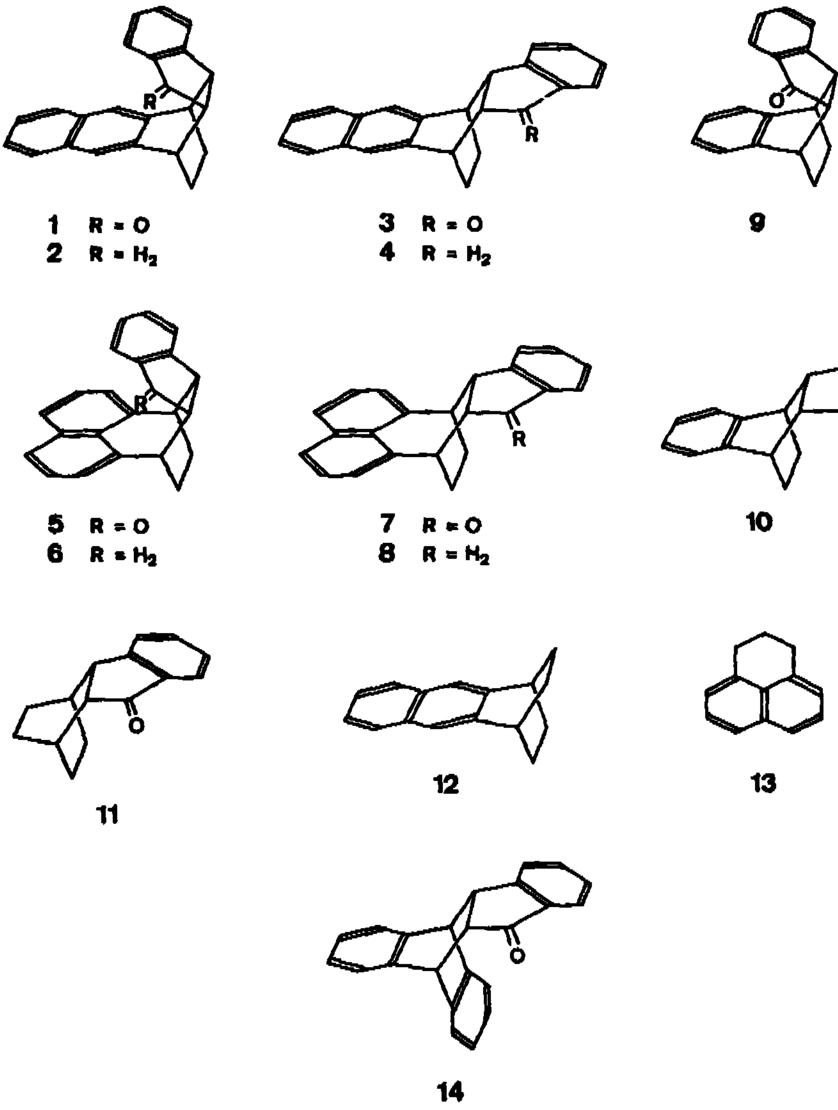
[1] Part of the doctoral thesis of *W. A.*, ETH Zürich, 1974.

Scheme 1. *Intramolecular energy transfer study: compounds with donor or acceptor chromophores and molecular* endo/exo *combinations*



and photobiological reasons. Most results are comprehensively summarized in recent reviews [1]. The model compounds studied in these investigations can be roughly divided on the basis of constitution into two classes, one comprising compounds with the chromophoric groups linked by aliphatic, conformationally flexible chains [2] and the other with rigid molecular frames holding donor and acceptor at a fixed distance [3] [4]. The studies were carried out by either spectroscopic methods [2a–c] [3] [4] or using the acceptor group as a photochemical probe [2d–f]. (Near-)quantitative transfers of singlet and/or triplet energy were observed for small spatial separations of donor and acceptor, and an appreciably lower efficiency in triplet energy transfer was found [3b] in cases where donor and acceptor were separated by near to *Ermolaev's* critical radii R_{DA} [5].

Among the compounds containing donor and acceptor groups in conformationally rigid geometric orientation, only orthogonal combinations – apart from tribenzotrypticene [4a] – have been investigated so far [4d–f], and no stereoisomeric models for direct comparisons have been available. The goal of our present work envisaged a study of stereoisomeric compounds in which the two groups are held in such positions as to avoid or to provide for head-on orbital overlap, respectively, and to explore possible differences in energy transfer within such pairs of stereoisomeric donor-acceptor combinations.

The choice of donor and acceptor in such a molecular combination should fulfil the following spectroscopic conditions: (i) the $S_0 \rightarrow S_1$ transition of the triplet donor should be energetically lower than that of the triplet acceptor and thus be amenable to selective excitation in the presence of the latter chromophore, (ii) a small $S_1 - T_1$ separation in the triplet donor in order to assure a high intersystem crossing yield (Φ_{isc}), (iii) a high phosphorescence quantum yield (Φ_p) of the triplet donor which should facilitate the observation of any residual donor phosphorescence in the presence of the triplet acceptor, (iv) the singlet donor/triplet acceptor must show fluorescence and phosphorescence, and (v) the acceptor T_1 state must lie sufficiently below that of the triplet donor to provide for an essentially irreversible triplet energy transfer. A combination of the 1-indanone and naphthalene chromophores adequately satisfies these conditions for triplet donor and acceptor, respectively. Indanone has its $S_0 \rightarrow S_1$ ($n \rightarrow \pi^*$) transition sufficiently separated from the aromatic absorption range, a quantitative $S \rightarrow T$ intersystem crossing, and a $\Phi_p = 0.56$ (total phosphorescence) in ether/isopentane/ethanol 5:5:2 (EPA) at 77°K [6]. Naphthalene exhibits both emission from S_1 and T_1 ($\Phi_{isc} \sim 0.6$ [7]) under the same conditions, and T_1 (naph) (with ^3L_a symmetry) is 15 kcal/mol lower than T_1 (ind) (*cf.* also Tables 1 and 2 and Fig. 6). The second triplet of naphthalene (with ^3B_b symmetry) is estimated at *ca.* 13 kcal/mol above T_1 (ind) and the transition $^3B_b \rightarrow {}^3L_a$ is symmetry-forbidden. Furthermore, indanone and naphthalene are photochemically reasonably stable.

Compounds **1**, **3**, **5** and **7** (*Scheme 1*) represent two pairs of stereoisomers, each with an indanone and a naphthalene moiety held in a conformationally rigid *endo/exo* orientation on a bicyclic hydrocarbon frame[2]. The change of the spatial orbital overlap of the chromophores within each pair, **1/3** and **5/7**, keeps the number of the remaining structural parameters constant. An eventual difference in the intramolecular triplet energy transfer between *endo* and *exo* isomer could thus be interpreted in terms of the exchange mechanism. Furthermore, the two pairs are formally interconvertible by an in-plane rotation of 90° of the naphthalene system. Any difference in triplet energy transfer as a consequence of this «rotational» isomerism could be indicative of a dipole-dipole interaction character of the transfer originating from a singlet contribution owing to spin-orbit coupling.

Additivity of the UV. absorptions of triplet donor and acceptor chromophores. – The aromatic absorption spectra of the naphthaleno ketones **1**, **3**, **5** and **7**

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[2] In a previous communication [8] we have briefly described a study of the intramolecular energy transfer in indanono naphthaleno *o*-benzeno compounds (*Scheme 2*: **15** and **17**). While the preliminary emission results in that series were similar to those reported in this work, we decided to replace the *o*-benzeno by the ethano bridge (→ **1**, **3**) in order to eliminate both any interpretative ambiguity arising from a possible participation of the *o*-benzeno system in the mixing of electronic states, and certain experimental difficulties caused by the low solubility of the benzeno derivatives.

are roughly composed of the sums of the extinctions of the individual indanono and naphthaleno chromophores. Thus, mixtures of the appropriate model compounds, **11**+**12** and **11**+**13**, gave the spectra of **1**/**3** and **5**/**7**, respectively, in reasonably good approximation (see Fig. 1 and 2)[3]. The extinctions of the carbonyl *n* → *π** bands, however, are appreciably greater in the *exo* naphthaleno ketones (**3** and **7**) and also, less pronounced, in the *exo* benzeno ketone (**10**) than in the *endo* isomers (**1**, **5**, **9**). Moreover, the *n* → *π** extinction coefficients of the naphthaleno ketones **3**, **5** and **7** are greater than those of the indanone **11**. These effects seem to indicate that the

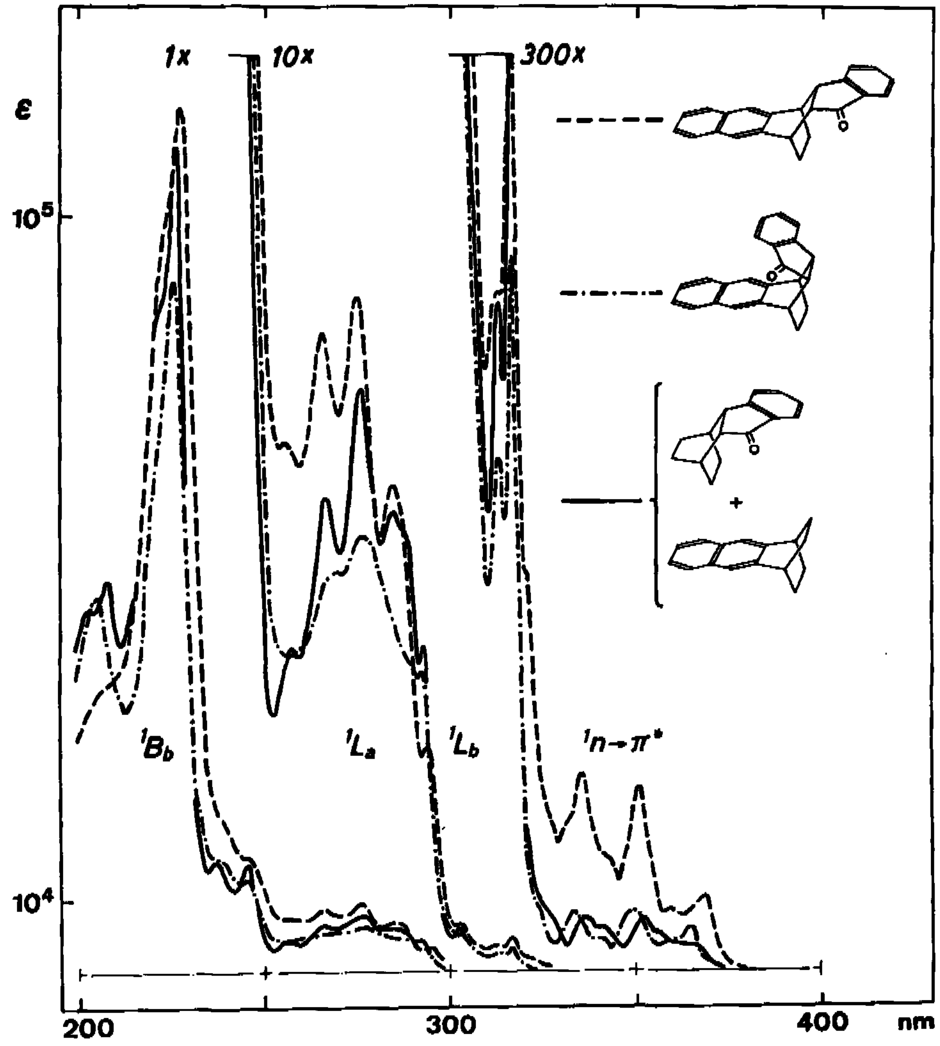

Fig. 1. *UV. absorption spectra of ketones* **1** *and* **3** *and of an equimolar mixture of* **11** + **12** *in iso-octane solutions* (Concentrations adjusted for quantitative comparison)

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[3] The different substitutions on naphthalene in the two pairs (2,3-*ortho* and *peri*) are reflected in a bathochromic shift of the ^1L_b (0–0) band in the *peri*-annelated ketones, *i.e.* S_1 (**5**, **7**) < S_1 (**1**, **3**).

$n \rightarrow \pi^*$ transition is somewhat less symmetry-forbidden owing to mixing of the carbonyl n orbital with the arylene π wavefunction, which process is more favorable in the *exo* configuration with coplanar donor and acceptor π systems than in the *endo* arrangement.

Despite this – relatively modest – deviation from strict additivity of the individual donor and acceptor absorptions in the naphthaleno ketones, strong electronic interactions, in particular such with charge-transfer character, are not apparent, and sufficiently meaningful independence of the two chromophores can *a priori* be assumed.

Emission properties of the triplet acceptor components. – The radiative properties of the naphthaleno acceptors were studied using the *endo/exo* hydrocarbon

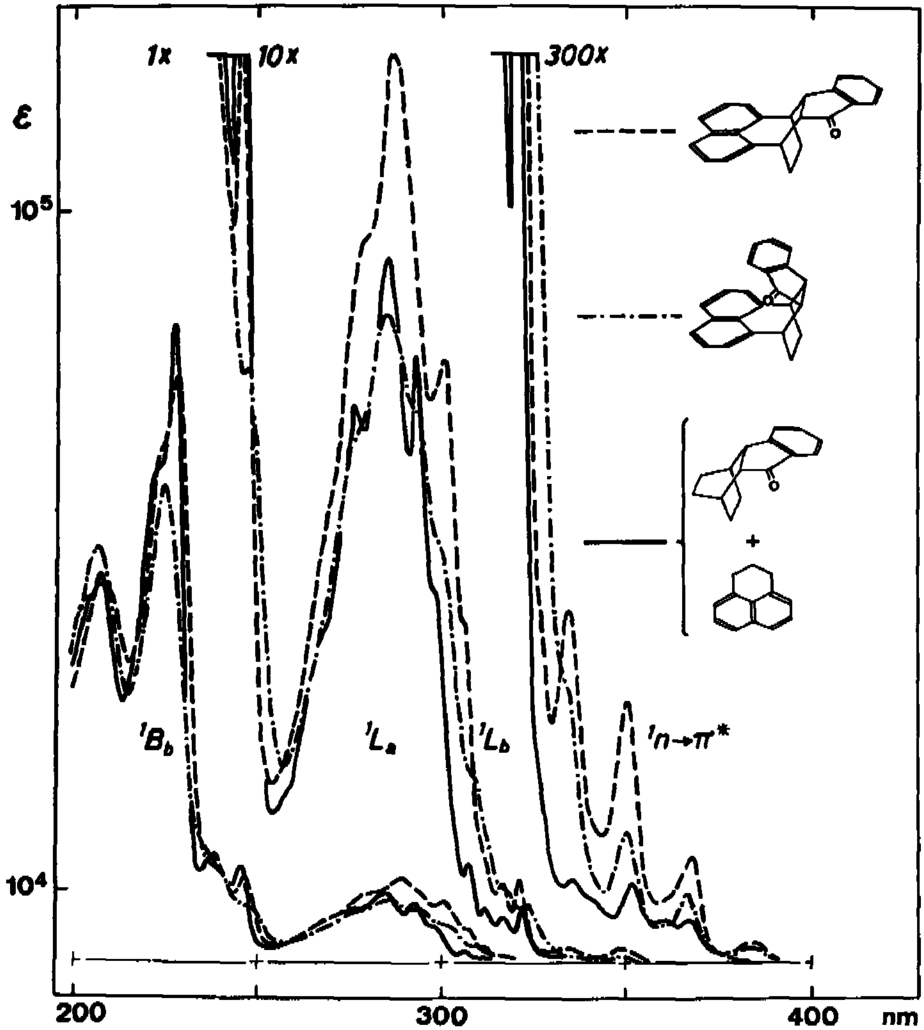

Fig. 2. *UV. absorption spectra of ketones* 5 *and* 7 *and of an equimolar mixture of* 11 + 13 *in iso-octane solutions* (Concentrations adjusted for quantitative comparison)

pairs **2**/**4** and **6**/**8** and comparing them with the annelated naphthalenes **12** and **13**, respectively. All compounds exhibited fluorescence and phosphorescence on irradiation in the ^1L_c band at *ca.* 315 nm and 77°K in EPA. A comparison of the emission data of these compounds with those of the parent naphthalene reveals some influence of the alkyl substitution on the emission properties, and in particular on phosphorescence (see Table 1). While the fluorescence quantum yields (Φ_f) are quite similar for naphthalene and for **2**, **4**, **6** and **8**, Φ_p is distinctly lower for the latter compounds. Alkyl substitution on naphthalene thus either lowers the S → T intersystem crossing tendency or enhances the non-radiative triplet decay. The differences within the *endo*/*exo* pairs are negligible, but Φ_p for the *peri*-annelated naphthalenes **6** and **8** is still lower than for the 2,3-*ortho*-annelated isomers. Furthermore, the triplet energies are *ca.* 1 kcal/mol smaller with *peri* substitution and greater with 2,3-*ortho* substitution than in the parent naphthalene, whereas only in the 2,3-*ortho* compounds the phosphorescence lifetime (τ_p) also differs, showing an increase of *ca.* 1 s over τ_p (naph).

Table 1. *Fluorescence and phosphorescence data of naphthalene and the hydrocarbons* **2**, **4**, **6**, **8**, **12**, *and* **13**a)

Compound	Fluorescence			Phosphorescence				
	0–0 Band (nm)	E_S (kcal/mol)	Φ_f	0–0 Band (nm)	E_T (kcal/mol)	τ_p (s)	Φ_p	Φ_f/Φ_p
Naphthalene	314.5	90.8	0.39b)	469	60.9c)	2.6c)	0.060b)	7
2	315.5	90.6	0.45	463.5	61.7	3.6	0.015	30
4	316	90.5	0.27	462.5	61.8	3.4	0.012	25
12	316	90.5	–	463	61.7	3.5	–	–
6	322	88.8	0.45	481	59.4	2.7	0.006	75
8	321.5	88.9	0.55	479	59.6	2.8	0.009	65
13	320.5	89.2	–	483.5	59.2	2.4	–	–

a) Excitation in the ^1L_b band at 77°K in EPA. b) Data from [9a]. c) These values are comparable to literature data; *cf.* [9].

Emission properties of the triplet donor chromophore. – The properties of the donor in the absence of acceptor were investigated with the indanono models **9**–**11** and **14**. As in 1-indanone, Φ_{isc} in all these compounds is practically quantitative in EPA at 77°K, and they exhibit a similar dual phosphorescence ascribed to simultaneous emission from both the n,π^* and π,π^* triplets, with the phosphorescence from the T(n,π^*) state as the predominant component when excited in the $n \rightarrow \pi^*$ absorption band at 340 nm (see Table 2 for a summary of the previously reported data [10])[4].

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[4] The n,π^* and π,π^* triplets of these indanones do not rapidly equilibrate at 77°K despite their energetic near-degeneracy, and they exhibit characteristically different phosphorescences which can be selectively generated under appropriately chosen conditions of excitation and detection; *cf. Amrein et al.* [10] and references therein.

Table 2. *Phosphorescence data of 1-indanone and the ketones* **9–11** *and* **14**[a])

Compound	Phosphorescence from T ($n,\pi^*/\pi,\pi^*$)		
	E_T (kcal/mol)	τ_p (ms)	Φ_p (tot)
1-Indanone	76.2/75.6	4.0/270	0.56
9	75.0/75.2	2.3/170	0.45
10	75.0/74.5	1.8/160	0.45
11	74.5/75.0	1.7/170	0.60
14	74.8/74.6	2.4/155	

[a]) Data taken from [10].

Energy transfer study with ketones 1, 3, 5, and 7. – Irradiation of the four ketones in either the carbonyl $n \rightarrow \pi^*$ or the aromatic absorption range, at 77°K in EPA, gave in each case total emission spectra which are essentially identical in shape, energy and lifetime with the phosphorescence spectra observed for the corresponding naphthaleno acceptors of the hydrocarbons **2**, **4**, **6**, and **8** (see Fig. 3 and 4 and Table 3). However, the quantum yields are markedly higher for the naphthaleno ketones by an average factor of 4 in the 2,3-*ortho*-substituted pair **1**/**3** and 9.5 in the *peri*-compounds **5**/**7**. No fluorescence was detected from these ketones at any excitation wavelength. The lack of any important qualitative dependence of the intramolecular energy transfer processes on the *endo*/*exo* stereoisomerism was further substantiated by the results of dynamic quenching experiments using 0.2M 1,3-pentadiene at room temperature. The photostationary *trans-cis* ratios of the diene obtained are

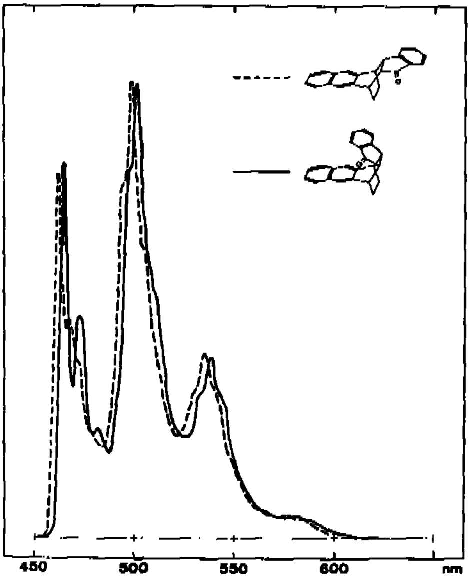

Fig. 3. *Total emission spectra* (*phosphorescence*) *of the* endo/exo *ketone pair* **1**/**3**

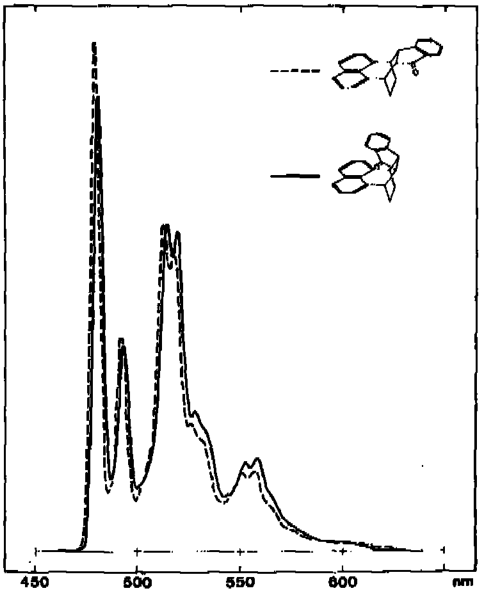

Fig. 4. *Total emission spectra (phosphorescence) of the* endo/exo *ketone pair* **5**/**7**

Table 3. *Phosphorescence data of the* endo/exo *ketone pairs* **1**/**3** *and* **5**/**7**a)

Compound	Phosphorescence				
	0–0 Band	E_T (kcal/mol)	τ_D (s)	Φ_p	χ b)
1	464.5	61.5	3.4	0.05	3
3	462.5	61.8	3.5	0.07	5
5	480	59.6	2.6	0.05	8
7	478	59.8	2.8	0.10	11

a) Irradiation at 340 nm and 77°K in EPA glass.

b) $\chi = \frac{\Phi_p\ (\text{ketone}/n \to \pi^*\ \text{excit.})}{\Phi_p\ (\text{hydrocarbon}/{}^1L_b\ \text{excit.})}$.

practically equal for the components of each pair of naphthaleno ketones (**1**: 1.72, **3**: 1.76, **5**: 1.85, **7**: 1.86), but differ from the ratio resulting with the benzeno ketones **9** (1.26) and **10** (1.29). Rather, they correspond closely to triplet sensitizer energies representative for those of the naphthalene moieties of **1**, **3**, **5**, and **7** (see Fig. 5)5).

The results of the emission and sensitized isomerization studies are evidence that, irrespective of the geometric donor-acceptor arrangement, (i) aromatic excitation of the naphthaleno ketones (irradiation at ≤320 nm only) is followed by singlet energy transfer from the naphthalene to the indanone chromophore, and (ii) the singlet-excited ketone undergoes intersystem crossing and acts as a triplet donor to the naphthalene moiety. To the extent that neither fluorescence from the naphthalene nor phosphorescence from the indanone partial structures are observed,

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5) For the method see *Hammond et al.* [11].

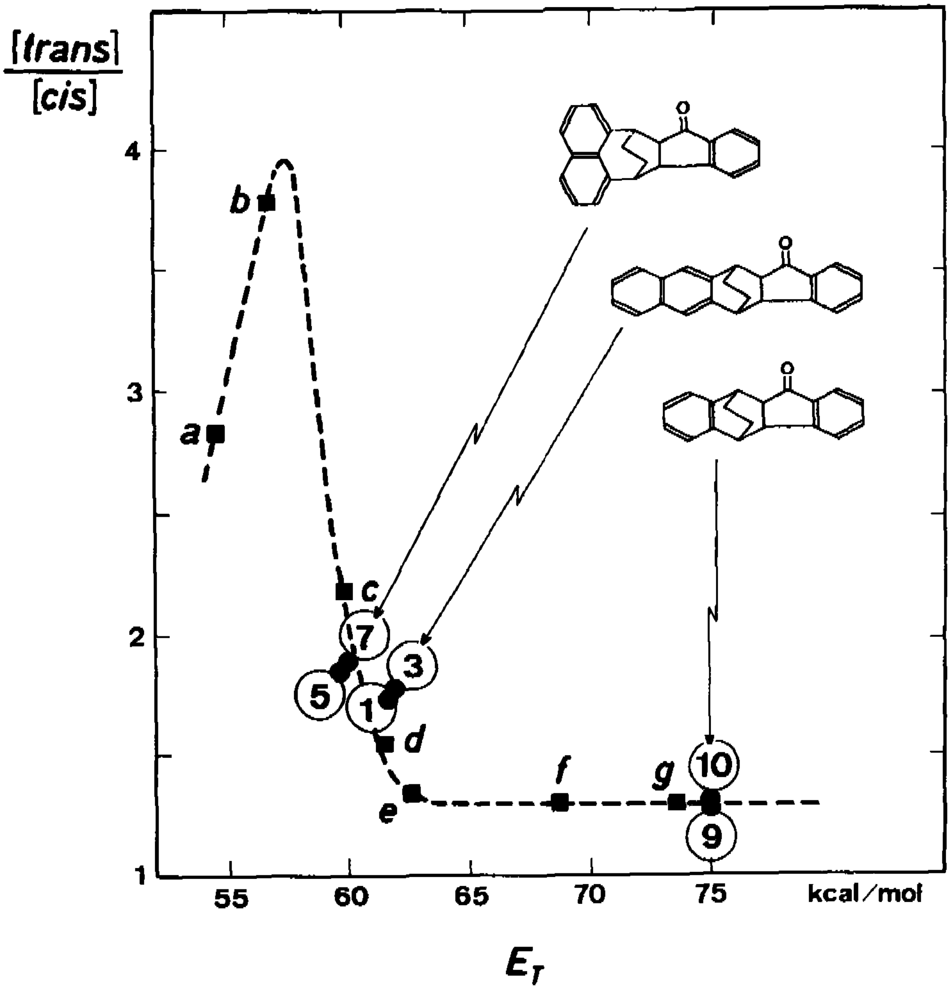

Fig. 5. *Sensitization with ketones* **1**, **3**, **5** *and* **7**: *photostationary* trans-cis *ratios of 1,3-pentadiene.* Irradiation at $\geqslant 322$ nm and room temperature in pentane solution. Reference sensitizers: *a* = *peri*-naphthindone, *b* = 1-acetonaphthone, *c* = 2-acetonaphthone, *d* = *Michler* ketone, *e* = 2-phenylchromone, *f* = benzophenone, *g* = acetophenone

these processes, as summarized in Fig. 6, are quantitative, and the limiting values for the rates of the radiationless energy transfers are at least three orders of magnitude greater than the rates of the competing radiative processes, *i.e.*, $k_{\mathrm{ET}}(^1\mathrm{A} \rightarrow {}^1\mathrm{D}) > 10^9\ \mathrm{s}^{-1} \gg k_f(\mathrm{A})$, and $k_{\mathrm{ET}}(^3\mathrm{D} \rightarrow {}^3\mathrm{A}) > 10^6\ \mathrm{s}^{-1} \gg k_p(\mathrm{A})$[6]. However, the values are probably substantially greater[7]. Based on the large energy gap between triplet donor and acceptor ($\Delta E_{\mathrm{T}} \sim 15$ kcal/mol), $k_{\mathrm{ET}}(^3\mathrm{D} \rightarrow {}^3\mathrm{A}) \sim 10^{10}\ \mathrm{s}^{-1}$ can be estimated, using a virtual acceptor concentration of *ca.* 5 mol/l (derived from an average donor-

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[6] The designations D (for triplet donor) and A (for triplet acceptor) are used henceforth for the indanone and naphthalene partial structures, respectively, in our compounds.

[7] *Morrison et al.* [2d] estimate $k_{\mathrm{ET}}(^3\mathrm{D} \rightarrow {}^3\mathrm{A}) \geqslant 10^8\ \mathrm{s}^{-1}$ for the intramolecular energy transfer in 1-phenyl-2-butene.

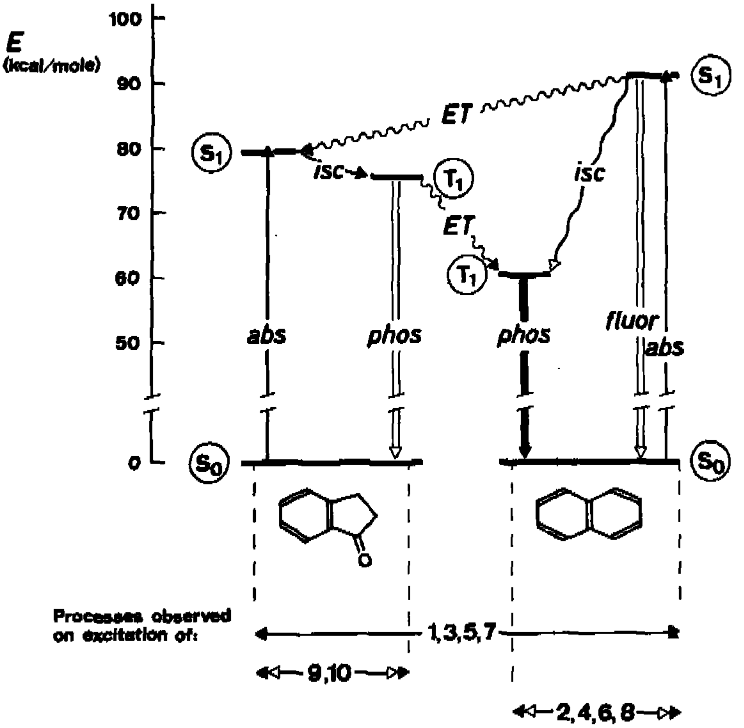

Fig. 6. *Intersystem crossing* (isc), *energy transfer* (ET), *and emission* (fluor, phos) *in 1-indanone, naphthalene, the ketones* **1**, **3**, **5**, **7**, **9**, *and* **10**, *and the hydrocarbons* **2**, **4**, **6**, *and* **8**

acceptor separation $R_{DA} \sim 4$ Å) and the bimolecular quenching constant $k_{QT} = 1.2 \cdot 10^9$ l/mol · s for the benzophenone-naphthalene system in benzene at 25° [12]. This relatively high value for $k_{ET}(^3D \rightarrow {}^3A)$ appears reasonable in the light of the substantially greater critical radii of 12–20 Å for 50% efficiency of intermolecular triplet energy transfer which have been determined by *Ermolaev* [5] by static quenching experiments. Furthermore, the exponential distance term in the *Dexter* equation for the exchange mechanism [13][8]) will strongly increase with small R_{DA} values and, together with the favorable spectral overlap integral in our naphthaleno ketones (Fig. 7), will render great $k_{ET}(^3D \rightarrow {}^3A)$ values plausible.

Competition between inter- and intra-molecular triplet energy transfer could be enforced in static quenching experiments with 2,5-dimethyl-2,4-hexadiene in EPA glass at 77° K, which were carried out with the ketones and hydrocarbons **14** (*Scheme 1*) and **15–19** (*Scheme 2*), the *o*-benzeno-bridged analogues of **1–4**, **9**, **10** and **12**. From the phosphorescence quenching data thus obtained the critical radii R_c were calculated and are summarized in Table 4[9]). The naphthalene parts of

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[8]) $k_{ET}(D^* \rightarrow A^*) = (2\pi/\hbar)\,[K \cdot \exp(-2R_{DA}/L)] \int_0^\infty P_D(\bar{\nu}) \cdot \varepsilon_A(\bar{\nu})\, d\bar{\nu}$, with K = energy constant, R_{DA} = distance between centres of donor and acceptor, L = average effective *Bohr* radius of electronic ground and excited states of donor and acceptor, $P_D(\bar{\nu})$ = emission spectrum of donor, $\varepsilon_A(\bar{\nu})$ = absorption spectrum of acceptor.

[9]) For the calculation of the R_c values (Table 4) the expressions $I_0/I_Q = \exp(\alpha \cdot [Q])$ and $R_c = \sqrt[3]{400 \cdot \alpha}$ described by *Perrin & Vavilov* [15] and *Ermolaev* [5], respectively, were used; I_0 and I_Q = intensities of donor phosphorescence without quencher and with quencher concentration [Q], respectively, and α = slope of linear plot $\ln(I_0/I_Q)$ *vs.* [Q].

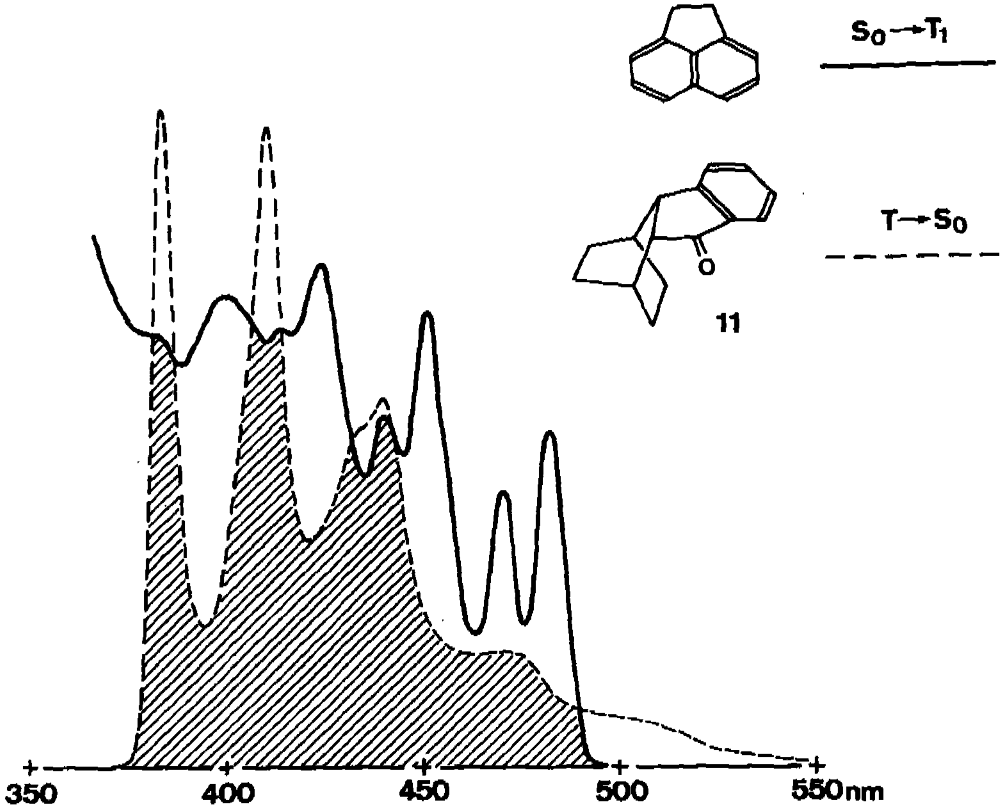


Fig. 7. *Spectral overlap in the naphthaleno ketones as exemplified by the S → T absorption spectrum of acenaphthene* (according to *Kearns et al.* [14]) *and the T → S total phosphorescence spectrum of ketone* **11** (on excitation at 340 nm)

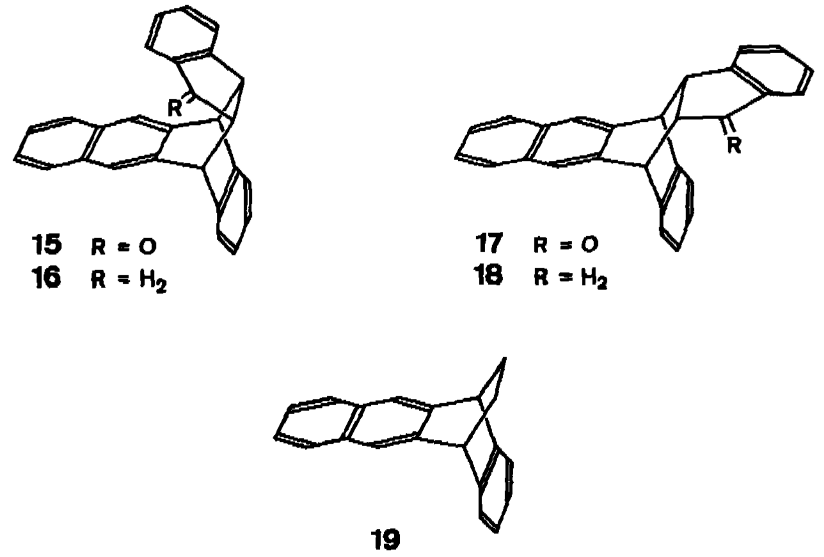
Table 4. *Static quenching experiments with compounds* **14–19** *and 2,5-dimethyl-2,4-hexadiene: critical radii R_c for 50% efficiency of intermolecular triplet energy transfer*[a])

	Hydrocarbon	R_c (Å)	Ketone	R_c (Å)
	19	16.4 ± 0.2		
exo:	**18**	16.3 ± 0.2	**17**	15.5 ± 0.2
endo:	**16**	15.4 ± 0.1	**15**	16.4 ± 0.2
			14	14.0 ± 0.05

[a]) Excitation in the ^1L_b band (hydrocarbons) and at 340 nm (ketones) at 77°K in EPA glass. For calculation of R_c see footnote 9.

the hydrocarbons **18** and **19** are similarly free of steric shielding and they possess the same R_c values, whereas in the *endo* compound **16** the protection by the indano group of one face against quenching by diene is reflected in a smaller R_c. Although the aromatic ketone in **14**, with the smallest R_c, proves to be a less efficient triplet donor than naphthalene in this series, its donor capacity toward external quencher can compete with intramolecular transfer in the *endo* compound **15** and thus compensates its steric inhibition effect sufficiently for placing **15** in the same R_c group as the hydrocarbons **18** and **19**. The 'active volume' of the *exo* ketone **17** again ranges between **14**

Scheme 2. *Static quenching experiments with 2,5-dimethyl-2,4-hexadiene : donor compounds (+ ketone* **14***)*



15 R = O
16 R = H_2

17 R = O
18 R = H_2

19

and **15**/**18**/**19**. As a consequence of the *exo* configuration in **17**, the competition between inter- and intra-molecular deactivation of the indanone system now results exclusively in competition with the quenching of the sterically unhindered naphthalene group.

Quantitative conclusions concerning the rate constants of the energy transfers observed here and a mechanistic differentiation of the intramolecular processes based on the interpretation of these static quenching results are not possible, however, as the latter reflect primarily the topologically determined relationship between donor and acceptor molecules.

The finding that the ketone donor consistently increases the naphthalene phosphorescence quantum yield more strongly in the exo *configuration than in the corresponding* endo *isomers* (see factors χ in Table 3) *is quite probably significant and requires that the triplet energy transfer is more efficient in the* exo *than in the* endo *configuration*[10]*.*

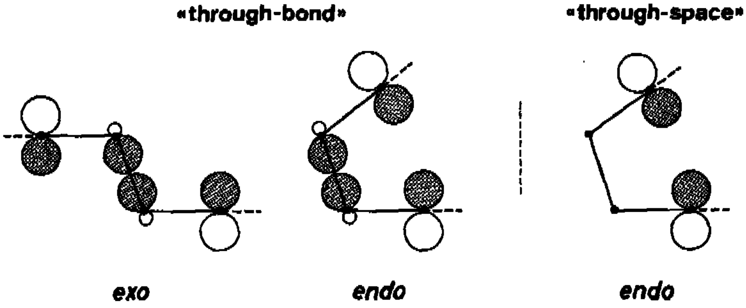


Fig. 8. *Through-σ-bond (in compounds* **1**, **3**, **5** *and* **7**) *and through-space interaction (in compounds* **1** *and* **5**) *between indanone and naphthalene chromophores*

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[10] This conclusion is subject to the validity of the assumptions that corrections of the χ factors of Table 3 for back-transfer and for radiationless deactivation of triplet naphthalene to ground state may be neglected here. Both assumptions appear reasonably safe in view of $\Delta E_T \sim 15$ kcal/mol and the invariance of τ_p within each hydrocarbon-ketone pair (*cf.* Tables 1 and 3), respectively.

We tentatively propose, as one possible explanation of this observation, that in both configurations an efficient through-σ-bond exchange transfer mechanism is operative, and that in the *endo* configuration an additional mechanism, *e.g.* one based on through-space interaction, competes with the population of the triplet naphthalene state. An estimate based on simple *Hückel* calculations of the ground state of the *endo*-ketone **5** (using the bond lengths and angles determined by X-ray diffraction analysis [16]) indicates that through-bond interaction may be of *ca.* fivefold greater importance than through-space orbital overlap in the *endo* case (*cf.* Fig. 8)[11].

Any process which might compete with the intramolecular triplet energy transfer must take place at some stage beyond that of the parent indanone triplet donor. With $\Phi_{\text{isc}}(^1\text{D}) \sim 1$ and $\Phi_{\text{p}} \sim 0.5$ (*cf.* Table 2), $k_{\text{isc}}(^3\text{D})$ can assume a maximum value of *ca.* $10^3\ \text{s}^{-1}$ and thus is substantially smaller than the estimated $k_{\text{ET}}(^3\text{D} \rightarrow {}^3\text{A})$ (*vide supra*). Consequently, the lower transfer efficiency in the *endo* compounds is to be ascribed rather to the transfer process, and the corresponding part of the diagram given in Fig. 6 requires a further refinement when applied to the *endo* compounds **1** and **5**. A weak intramolecular exciplex, T(DA) in Fig. 9, would introduce a mechanistically plausible route for additional radiationless energy dissipation specific to through-space interaction in the *endo* configuration. The formation of such a weak exciplex is anticipated to involve strong coupling with vibrational states of the

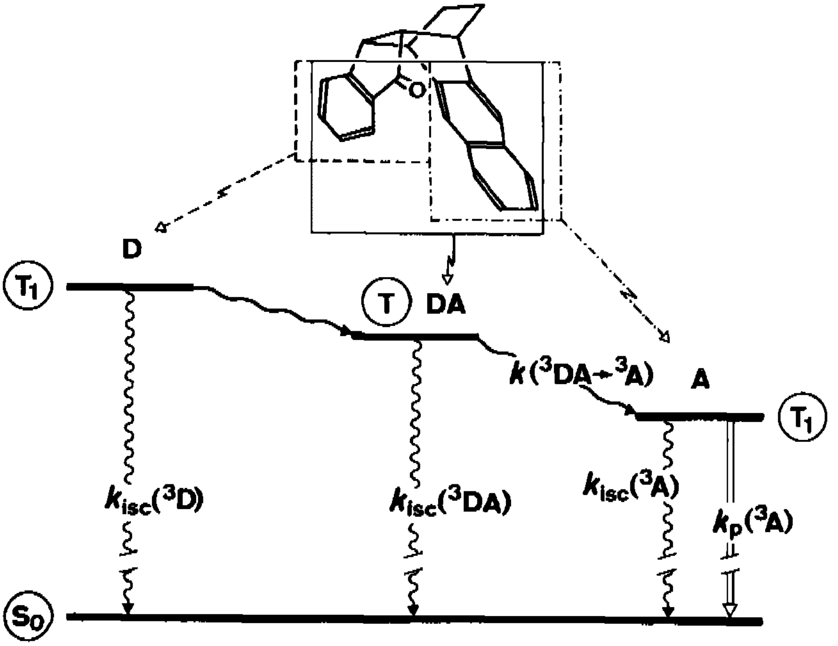

Fig. 9. *Intervention of a weak intramolecular exciplex in the* endo *triplet energy transfer introducing a route for energy wasting in the ketone* **1**

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[11] We thank Professor *R. Gerdil* for helpful discussions on this point. Work is currently in progress to probe experimentally the possibility of through-bond interaction in the ground state.

entire molecular skeleton through angle deformation between the donor and acceptor planes, concurrently favoring radiationless deactivation to ground state, $k_{isc}(^3DA)$, at this level. Triplet energy transfer *via* exciplex would thus explain satisfactorily the observed energy wasting, provided that $k(^3DA \rightarrow {}^3A)$ and $k_{isc}(^3DA)$ are of a similar order of magnitude[12]).

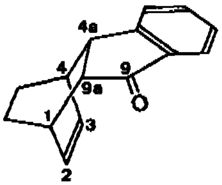
Other attempts to rationalize the transfer results, *e.g.* based on dipole-dipole interaction (by extension of the *Förster* concept to the donor-acceptor triplet term through spin-orbit coupling with singlet states [17]) and on a correlation of the triplet transfer efficiency with the orientation of donor and acceptor planes [18][13]), adequately account for the observed *exo* > *endo* difference in efficiency. They fail, however, to provide a mechanism for an *endo*-specific competitive radiationless deactivation.

Financial support by the *Fonds National Suisse de la Recherche Scientifique* and *Firmenich S.A.*, Geneva, is gratefully acknowledged.

Experimental Part

Compounds. – For general remarks consult the accompanying paper [20] which describes the synthesis of compounds **1–10** and **12**. The hydrocarbons **13** [21] and **19** [22] are described in the literature.

1,2,3,4,4a,9a-Hexahydro-1,4-ethano-fluoren-9-one (**11**). A mixture of 3.20 g freshly distilled indenone [23], 50 mg trinitrobenzene and 3 ml 1,3-cyclohexadiene was heated to 50° for three days and then taken up in cold hexane. After decanting from insoluble material and evaporation of the solvent, the residue was treated with charcoal in MeOH and chromatographed with benzene/ethyl acetate 25:1 : 3.8 g (59%) endo-*1,4,4a,9a-tetrahydro-1,4-ethano-fluoren-9-one* (**20**). The analytical sample was distilled at 120°/0.01 Torr. – IR.: 763 s, 1064 m, 1160 m, 1258 m, 1294 m, 1340 m, 1470 m, 1613 m, 1715 s, 2880 m, 2915 m, 2945 m, 3060 m. – NMR.: 1.24–1.90/*m*, two H_2—C; 2.69/*d*×*d*, $J_{1,9a} = 3.5$, $J_{4a,9a} = 7.5$, H—C(9a); 2.93–3.26/*m*, H—C(1 and 4); 3.40/*d*×*d*, $J_{4,4a} = 3.0$, $J_{4a,9a} = 7.5$, H—C(4a); 5.71 + 5.96/*AA'*MM', double resonance with 2.93–3.26 → *AB*, $J_{2,3} = 8.0$, H—C(2 and 3); 7.20–7.82/*m*, four arom. H. – MS.: 210 ($C_{15}H_{14}O^+$, 27%), 181 (7%), 165 (5%), 133 (10%), *132*, 131 (19%), 80 (97%), 79 (36%).



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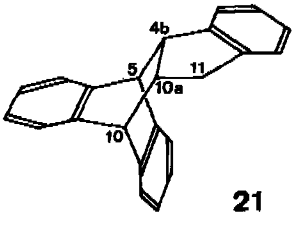

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[12] Experimental evidence in support of the intramolecular exciplex mechanism considered above is not available at present, and we are not aware of firmly established analogies in the literature. However, observations reported, *e.g.*, for tribenzotrypticene [4a] may be interpreted on the basis of similar weak exciplex and/or vibrational interactions.

[13] The *exo* > *endo* difference in triplet energy transfer efficiency follows, *e.g.*, directly from the application of the expression emanating from several investigations of the dependence of the triplet energy transfer on donor-acceptor orientation [18] which, for the greater part, are based experimentally on studies of solid solutions of benzophenone and phenanthrene by the photoselection method [19]: $k_{ET}(^3D \rightarrow {}^3A)\,(\varphi) = k^0_{ET}(^3D \rightarrow {}^3A) \cdot \cos^m\varphi$ [18c], with φ = angle between donor and acceptor planes, $k^0_{ET}(^3D \rightarrow {}^3A)$ = rate constant of energy transfer at optimum φ, m = constant (0–2) determining the response of $k_{ET}(^3D \rightarrow {}^3A)\,(\varphi)$ to changes of φ.

Hydrogenation of 2.50 g **20** with 500 mg Pd/C (10%) in 25 ml ethyl acetate gave, after crystallization from hexane, 1.55 g (62%) of *ketone* **11**; m.p. 61–63°. – IR.: 720 m, 1105 m, 1260 m, 1287 m, 1470 m, 1612 m, 1717 s, 2880 m, 2920 m, 2950 s, 3080 w. – NMR.: 1.04–1.96/*m*, four H_2—C; 2.04–2.34/*m*, H—C(1 and 4); 2.66/*d*×*d*, $J_{1,9a} = 3.5$, $J_{4a,9a} = 8.4$, H—C(9a); 3.39/*d*×*d*, $J_{4,4a} = 3.8$, H—C(4a); 7.25–7.85/*m*, four arom. H. – UV. (isooctane): 209 (23800), 238 (12900), 246 (11900), 276 (1600) 284 (2600) 294 (3300) 314 (27), 327 (34), 336 (37), 351 (29), 368 (12). – MS.: 212 ($C_{15}H_{16}O^+$, 48%), 158 (16%), *132*, 131 (32%).

4b,5,10,10a-Tetrahydro-5,10-o-benzeno-benzo[b]*fluoren-11-one* (**14**)[14]. Addition of 3.5 g indene to 1.78 g anthracene in an autoclave under N_2 at 200° for 3.5 h gave, after chromatography with petroleum ether and distillation at 140°/0.01 Torr, an 85% yield of *4b,5,10,10a-tetrahydro-5,10-o-benzeno-11*H-*benzo*[b]*fluorene* (**21**), m.p. 115° (cryst. from benzene/EtOH). – IR. ($CHCl_3$): 942 m, 1025 s, 1119 s, 1170 s, 1464 s, 1485 s, 1588 m, 1909 w, 1948 w, 2840 m, 3000 s, 3060 s. MS.: *178* (M^+ – indene), 152, 116.

$C_{23}H_{18}$ (294.37) Calc. C 93.84 H 6.16% Found C 93.81 H 6.18%

Oxydation of 10 g **21** with 30 g $Na_2Cr_2O_7$ in 5 ml 10% aqueous H_2SO_4 and 80 ml AcOH for 3 h at reflux temp. gave, after chromatography with petroleum ether/$CHCl_3$ 3:1 and crystallization from $CHCl_3$/petroleum ether, a 75% yield of *ketone* **14**, m.p. 204.5–205°. – IR.: 660 w, 1206 w, 1278 m, 1455 m, 1464 m, 1602 m, 1712 s, 2940 m, 3020 m, 3065 m. – NMR.: 3.10/*d*×*d*, $J_{4b,10a} = 7.5$, $J_{10,10a} = 3.5$, H—C(10a); 3.80/*d*×*d*, $J_{4b,5} = 3.2$, $J_{4b,5} = 7.5$, H—C(4b); 4.62/*d*, $J_{4b,5} = 3.2$, H—C(5); 5.80/*d*, $J_{10,10a} = 3.5$, H—C(10); 6.70–7.60/*m*, twelve arom. H. – UV. (dioxane): 246 (11000), 266 (2350), 273 (2500), 288 (2200), 297 (2100); ($CHCl_3$): 330 (70), 354 (25). – MS.: 308 (M^+, 0.1%), 179 (15%), *178*, 177 (4%), 176 (5%), 152 (3%), 138 (2%).

$C_{23}H_{16}O$ (308.36) Calc. C 89.58 H 5.23% Found C 89.58 H 5.29%

endo- *and* exo-*13-Oxo-4b,5,12,12a-tetrahydro-5,12-o-benzeno-indeno*[2,3-b]*anthracenes* **15** *and* **17**[14][15]. Freshly distilled indenone [23] was added dropwise to a solution of 2.28 g naphthacene in 30 ml boiling decalin until the solution had turned colorless (*ca.* 4.5 g ketone). After 30 min of reflux the mixture was cooled to 0°. 2.68 g (75% yield) of a crystalline mixture of **15** and **17** precipitated, which was filtered through neutral Al_2O_3 (act. II) in CH_2Cl_2. Chromatography in benzene on 250 g silicagel impregnated with 3% $AgNO_3$ furnished 194 mg **15**, 795 mg **17** and 665 mg of a mixed fraction.

15: m.p. 217–218° (cryst. from hexane/CH_2Cl_2). – IR. ($CHCl_3$): 839 w, 885 m, 1094 w, 1125 w, 1280 m, 1462 m, 1478 m, 1603 m, 1704 s, 2935 m, 2995 m, 3030 m. – NMR.: 3.15/*d*×*d*, $J_{4b,12a} = 7.6$, $J_{12,12a} = 3.6$, H—C(12a); 3.85/*d*×*d*, $J_{4b,5} = 3.2$, $J_{4b,12a} = 7.6$, H—C(4b); 4.71/*d*, $J_{4b,5} = 3.2$, H—C(5); 4.88/*d*, $J_{12,12a} = 3.6$, H—C(12); 6.86–7.80/*m*, fourteen arom. H. – MS.: 358 (M^+, 1%), 229 (18%), *228*, 226 (9%). – UV. ($CHCl_3$): 320 (530), 342 (78), 356 (36); (EtOH); 234 (67000), 258 (12000), 266 (8000), 272 (6900), 280 (5300), 293 (3500).

$C_{27}H_{18}O$ (358.44) Calc. C 90.47 H 5.06% Found C 90.50 H 5.10%

17: m.p. 284–285° (cryst. from hexane/CH_2Cl_2). – IR. ($CHCl_3$): 839 w, 889 m, 1128 w, 1150 w, 1282 m, 1463 m, 1586 m, 1603 m, 1704 s, 2935 m, 2990 m, 3030 m. – NMR.: 3.15/*d*×*d*, $J_{4b,12a} = 7.6$, $J_{12,12a} = 3.6$, H—C(12a); 3.86/*d*×*d*, $J_{4b,5} = 3.2$, $J_{4b,12a} = 7.6$, H—C(4b); 4.73/*d*, $J_{4b,5} = 3.2$, H—C(5); 4.91/*d*, $J_{12,12a} = 3.6$, H—C(12); 6.65–6.98 and 7.02 7.88/2 *m*, fourteen arom. H. – MS.: 358 (M^+, 1%), 229 (18%), *228*, 226 (9%). – UV. ($CHCl_3$): 320 (510), 339 (107), 357 (38); (EtOH): 238 (90000), 267 (10500), 279 (8600), 288 (6000), 297 (2900).

$C_{27}H_{18}O$ (358.44) Calc. C 90.47 H 5.06% Found C 90.17 H 5.07%

endo- *and* exo-*4b,5,12,12a-Tetrahydro-5,12-o-benzeno-13*H-*indeno*[2,3-b]*anthracenes* **16** *and* **18**[14][15]. – a) Diels-Alder *addition of indene and naphthacene*. A solution of 2.28 g naphthacene and

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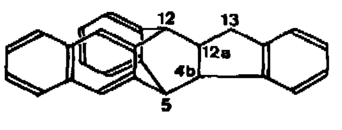
[14] Compounds **14–18** were prepared for the first time by *D. Karanatsios* (*cf.* [8]).

[15] Numbering of the 4b,5,12,12a-tetrahydro-5,12-*o*-benzeno-13*H*-indeno[2,3-*b*]anthracene system:



4 ml indene in 10 ml decalin was refluxed under N_2 for 2 h, then cooled, diluted with CH_2Cl_2 and filtered through neutral Al_2O_3 (act. I). 3.40 g (99% yield) of a mixture of **16** + **18** were obtained. Chromatography in benzene/hexane 3:2 on 367 g silicagel impregnated with 3% $AgNO_3$ afforded 593 mg **16**, 1.215 g **18** and 1.50 g of a mixed fraction.

16: m.p. 190–191° (cryst. from hexane). – IR.: 880 m, 889 m, 950 w, 1020 w, 1452 m, 1460 m, 1478 m, 1485 m, 1609 w, 2835 w, 2930 m, 3040 m. – NMR.: 2.60/*m*, H–C(12a); 2.90–3.28/*m*, H_2–C(13); 3.82/*d*×*d*, $J_{4b,5} = 2.8$, $J_{4b,12a} = 8.5$, H–C(4b); 4.31/*d*, $J_{12,12a} = 2.5$, H–C(12); 4.58/*d*, $J_{4b,5} = 2.8$, H–C(5); 6.58–7.70/*m*, fourteen arom. *H*. – MS.: 344 (*M*+, 0.1%), *229* (18%), *228*, 226 (10%), 202 (2%), 116 (3%), 115 (3%). – UV. ($CHCl_3$): 305 (620), 319 (590); (EtOH): 233 (65000), 260 (6100), 270 (8200), 276 (7600), 290 (3300).

$C_{27}H_{20}$ (344.43) Calc. C 94.15 H 5.85% Found C 94.25 H 5.93%

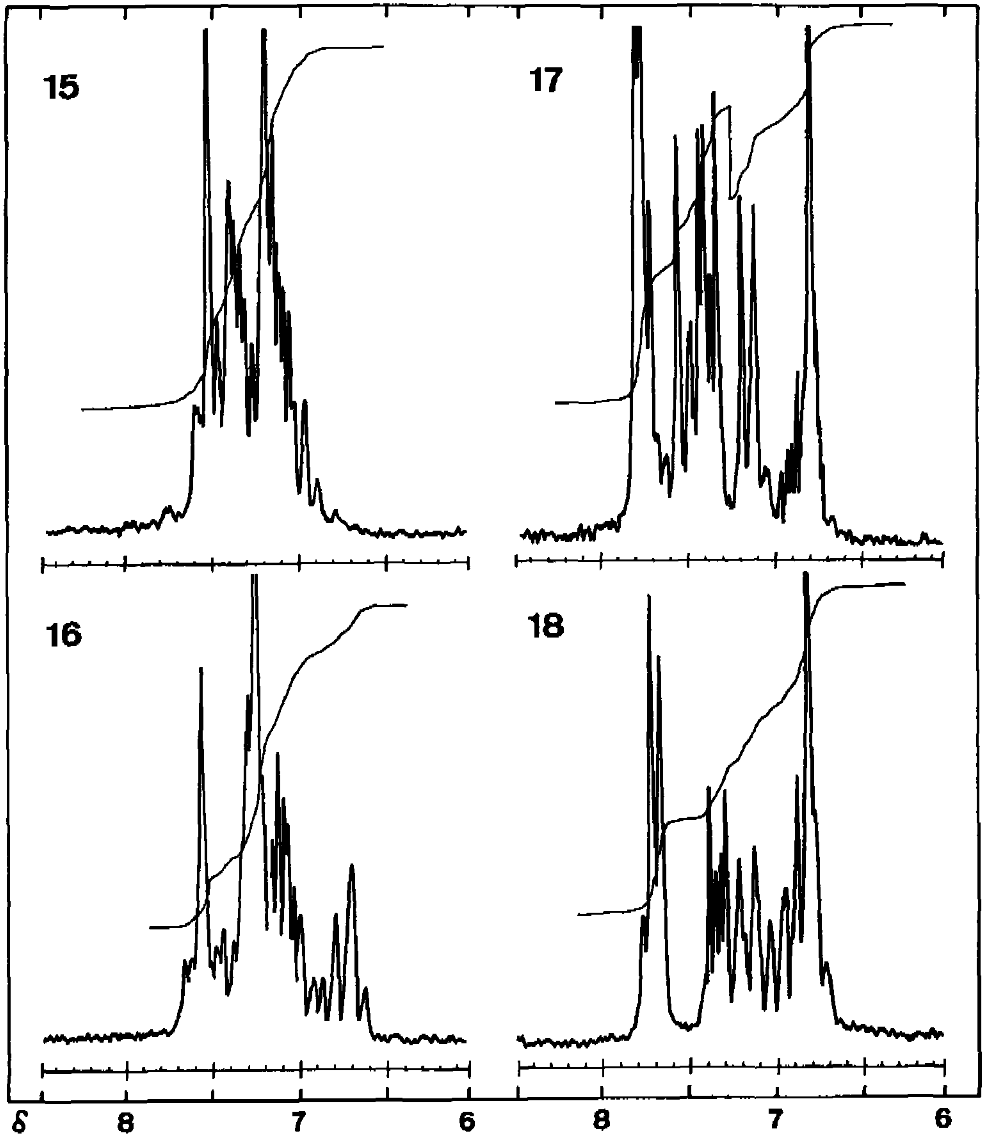


Fig. 10. *NMR. spectra of compounds* **15–18**: *aromatic proton patterns*

18: m.p. 222–223° (cryst. from hexane). – IR.: 887 m, 950 w, 1022 w, 1460 m, 1478 m, 1501 m, 1607 w, 2925 m, 2990 m, 3030 m. – NMR.: 2.55/*m*, H—C(12a); 2.90–3.28/*m*, H_2—C(13); 3.80/*d* × *d*, $J_{4b,5}$ = 3.0, $J_{4b,12a}$ = 7.8, H—C(4b); 4.33/*d*, $J_{12,12a}$ = 2.5, H—C(12); 4.58/*d*, $J_{4b,5}$ = 3.0, H—C(5); 6.78–7.45 and 7.62–7.84/2 *m*, fourteen arom. H. – MS.: 344 (M^+, 0.1%), 229 (18%), *228*, 266 (10%), 202 (2%), 116 (3%), 115 (3%). – UV. ($CHCl_3$): 306 (700), 320 (650); (EtOH): 235 (88000), 259 (7800), 269 (10500), 277 (9000), 291 (4500).

$C_{27}H_{20}$ (344.43) Calc. C 94.15 H 5.85% Found C 94.26 H 5.82%

b) Huang-Minlon *reduction of* **17**. A solution of 36 mg **17** in 2 ml ethylene glycol, 3 ml EtOH and 1 ml N_2H_4, H_2O was refluxed for 4 h under N_2. 200 mg of finely powdered KOH were then added to the cooled mixture. The volatile components were distilled off until the reflux temp. had reached *ca.* 200°. The work-up after 3 h reflux, filtration of the crude product in CH_2Cl_2 through neutral Al_2O_3 (act. I) and chromatography in benzene gave 30.5 mg (88% yield) **18**; m.p. 222–223° after crystallization from hexane (identification by mixed m.p., IR. and TLC. impregnated with $AgNO_3$).

endo/exo *Assignments to Compounds* **15–18** *by NMR*. The keto group in **15** and **17** quite generally deshields the aromatic indanone *ortho* proton and shields anisotropically one aromatic proton of the naphthaleno (in **15**) or the benzeno group (in **17**). In the hydrocarbons **16** and **18** the eight benzeno protons and the two naphthaleno β-protons appear at relatively high field, and the four naphthaleno α-protons are at lower field. In the *endo*-ketone **15** one of these latter lowfield protons is shifted upfield which, together with the downfield shift of the upfield indanone *ortho* proton, results in a narrower aromatic proton pattern in the *endo*-ketone **15** than in the corresponding hydrocarbon **16**. Alternatively, in the *exo*-ketone **17** the additional anisotropic shielding of one

Table 5. *Triplet sensitization of 1,3-pentadiene: phosphorescence data of sensitizers in EPA glass at 77° K and photostationary* trans/cis *ratios in pentane at 20°* [a])

Sensitizer	Phosphorescence			Sensitized diene isomerization			
	0–0 band	E_T	τ_p	concentration of sensitizer	concentration of diene	irradiation time [b])	*trans/cis* [c])
	(nm)	(kcal/mol)	(s)	(M)	(M)	(h)	
Perinaphthindone (*a*)	525	54.5	0.075	$1.60 \cdot 10^{-3}$	0.20	40	2.83 ± 0.03
1-Acetonaphthone (*b*)	503	56.8	0.137	$2.35 \cdot 10^{-3}$	0.20	24	3.78 ± 0.03
5	[d])	[d])	[d])	$0.13 \cdot 10^{-3}$	0.07	80	1.85 ± 0.04
2-Acetonaphthone (*c*)	478	59.8	0.93	$2.35 \cdot 10^{-3}$	0.20	24	2.16 ± 0.05
7	[d])	[d])	[d])	$0.90 \cdot 10^{-3}$	0.20	18	1.86 ± 0.04
Michler Ketone (*d*)	465	61.5	0.13	*ca.* 10^{-3}	0.20	18	1.53 ± 0.03
1	[d])	[d])	[d])	$0.58 \cdot 10^{-3}$	0.20	80	1.72 ± 0.01
3	[d])	[d])	[d])	$0.94 \cdot 10^{-3}$	0.20	40	1.76 ± 0.01
2-Phenylchromone (*e*)	457	62.5	0.425	$1.80 \cdot 10^{-3}$	0.20	24	1.33 ± 0.01
Benzophenone (*f*)	412	68.5	0.0047	$1.65 \cdot 10^{-3}$	0.20	18	1.30 ± 0.01
Acetophenone (*g*)	392	73.5	~0.004	$4.10 \cdot 10^{-2}$	0.10	5	1.30 ± 0.04
9		[e])	[e])	$0.85 \cdot 10^{-3}$	0.20	34	1.26 ± 0.03
10		[e])	[e])	$1.54 \cdot 10^{-3}$	0.20	36	1.29 ± 0.03

[a]) *Cf.* also Fig. 5. [b]) Four sample solutions each with *cis*- and *trans*-1,3-pentadiene were run with each sensitizer. Irradiations were conducted until the average differences in percentage diene composition between the *cis* and *trans* runs were smaller than 1%. [c]) Experimental standard deviation < ± 0.5% *trans* diene. [d]) See Table 3. [e]) See Table 2.

upfield benzeno proton is practically compensated by the deshielding of the upfield indanono *ortho* proton, and the widths of the aromatic proton pattern are almost the same in the *exo*-compounds **17** and **18** (see Fig. 10).

Instrumentation for absorption and emission spectroscopy. – The *UV. absorptions* (Fig. 1 and 2) were measured on a *Beckman* ACTA III spectrophotometer. – A detailed description of the instrument and techniques employed for *phosphorescence* measurements has been given in [20]. Supplementary informations: *Fluorescence* (total emission) at 77° K was recorded with the phosphoroscope and the shutter removed from the light path. Luminescence *quantum yields* are based on benzophenone ($\Phi_p = 0.59$ [9]) and naphthalene ($\Phi_f = 0.39$ [9]) as the references for the phosphorescence of the ketones (excitation at *ca.* 340 nm) and the fluorescence of the hydrocarbons (excitation in the ^1L_b band), respectively. The phosphorescence quantum yields of the hydrocarbons **2**, **4**, **6** and **8** were determined by direct comparison with Φ_p of the corresponding ketones (**1**, **3**, **5**, **7**). The reproducibility of all measurements (Tables 1, 2 and 3, Fig. 3, 4 and 7) is better than ±10%.

Photostationary *trans-cis* ratios of 1,3-pentadiene on sensitization. – Experimental conditions and results including phosphorescence data of the sensitizers are summarized in Table 5 (*cf.* also Fig. 5). The samples solutions were irradiated in an argon atmosphere in Pyrex tubes of 1.2 ml content in a merry-go-round apparatus equipped with a 250 W *Philips* Hg medium-pressure lamp placed in a water-cooled Pyrex finger surrounded by a cylindrical filter compartment (i.d. 1 cm) filled with acetone (wavelength cut-off $\leqslant$ 322 nm). The *trans-cis* ratios of 1,3-pentadiene were determined by gas chromatography using steel columns (4 mm × 4 m) packed with chromosorb G/5% (benzyl cyanide/$AgNO_3$ 2:1); temperatures 15° (column) and 50° (injector); carrier gas 50 ml helium/min; flame ionization detector; electronic peak area integration; retention times 5.6 min for *trans-* and 7.0 min for *cis*-diene. Blind runs with 0.2 M *cis-* and *trans*-diene without sensitizer gave less than 2% isomerization after 80 h irradiation.

Determination of the R_c values of 14–19. – The phosphorescence intensity I (measured at the maximum emission band) of compounds **14–19** in EPA glass at 77° K (concentration $2.5 \cdot 10^{-5}$ M[16])) was determined as a function of quencher concentration [Q] (0–0.15 M 2,5-dimethyl-2,4-hexadiene[16])). Excitation wavelength: 345 nm for the ketones **14**, **15** and **17**, 290 nm for the hydrocarbons **16**, **18** and **19**. A linear plot for ln $(I_0/I_Q)/[Q]$ was obtained in each case, with $\alpha = 6.8 \pm 0.05$ (**14**), 11.0 ± 0.4 (**15**), 9.1 ± 0.2 (**16**), 9.2 ± 0.4 (**17**), 10.8 ± 0.4 (**18**), 11.0 ± 0.3 l/mol (**19**) (experimental standard deviations from the scattering of all measured values)[9]). For the R_c values see Table 4.

The elemental analyses were carried out in the microanalytical laboratory of ETH Zurich under Mr. *W. Manser*. The NMR. and mass spectra were run by Dr. *U. Burger* and Professor *A. Buchs* (University of Geneva), respectively.

REFERENCES

[1] *N. Filipescu* in 'Molecular Luminescence', *E. C. Lim*, ed., Benjamin, New York 1969, p. 697; *A. A. Lamola* in 'Energy Transfer and Organic Photochemistry', *P. A. Leermakers & A. Weissberger*, eds., Interscience Publ., New York 1969, p. 70; *J. B. Birks*, 'Photophysics of Aromatic Molecules', Wiley-Interscience, London 1970, p. 594.

[2] a) *O. Schnepp & M. Levy*, J. Amer. chem. Soc. *84*, 172 (1962); b) *A. A. Lamola, P. A. Leermakers, G. W. Byers & G. S. Hammond*, ibid. *85*, 2670 (1963); *87*, 2322 (1965); c) *D. E. Breen & R. A. Keller*, ibid. *90*, 1935 (1968); d) *H. Morrison & R. Peiffer*, ibid. *90*, 3428 (1968); e) *D. O. Cowan & A. A. Baum*, ibid. *92*, 2153 (1970); *93*, 1153 (1971); f) *C. S. Nakagawa & P. Sigal*, J. chem. Physics *53*, 2993 (1970); g) *A. A. Lamola*, J. Amer. chem. Soc. *92*, 5045 (1970).

[3] a) *S. A. Latt, H. T. Cheung & E. R. Blout*, J. Amer. chem. Soc. *87*, 995 (1965); b) *R. A. Keller & L. Dolby*, ibid. *89*, 2768 (1967).

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[16] Concentration not corrected for volume contraction of the sample solutions.

[4] a) *M. S. DeGroot & J. H. Van der Waals*, Mol. Physics *6*, 545 (1963); b) *R. A. Keller*, J. Amer. chem. Soc. *90*, 1940 (1968); c) *J. A. Hudson & R. M. Hedges* in 'Molecular Luminescence', Benjamin, New York 1969, p. 667; d) *N. Filipescu & J. R. De Member*, Tetrahedron *24*, 5181 (1968); J. Amer. chem. Soc. *90*, 6425 (1968); e) *A. A. Lamola*, ibid. *91*, 4786 (1969); f) *N. Filipescu, J. R. De Member & F. L. Minn*, ibid. *91*, 4169 (1969); *N. Filipescu & J. M. Menter*, J. chem. Soc. (B) *1969*, 616; *J. M. Menter & N. Filipescu*, ibid. *1970*, 464; *J. R. Buntig & N. Filipescu*, ibid. *1970*, 1498, 1750; g) *H. E. Zimmerman & R. D. McKelvey*, J. Amer. Soc. *93*, 3638 (1971).

[5] *V. L. Ermolaev*, Opt. Spectroscopy *6*, 417 (1959).

[6] *N. C. Yang & S. Murov*, J. chem. Physics *45*, 4358 (1966).

[7] *A. R. Horrocks & F. Wilkinson*, Proc. Roy. Soc. *A 306*, 257 (1968); *K. Sandros*, Acta chem. Scand. *23*, 2815 (1969).

[8] *W. Amrein, D. Karanatsios & K. Schaffner*, Chimia *24*, 28 (1970).

[9] a) *E. H. Gilmore, G. E. Gibson & D. S. McClure*, J. chem. Physics *20*, 829 (1952); b) *V. L. Ermolaev*, Soviet Phys. Usp. *6*, 333 (1963).

[10] *W. Amrein, I.-M. Larsson & K. Schaffner*, Helv. *57*, 2519 (1974).

[11] *G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt & C. Dalton*, J. Amer. chem. Soc. *86*, 3197 (1964).

[12] *G. Porter & F. Wilkinson*, Proc. Roy. Soc. *A 264*, 1 (1964).

[13] *D. L. Dexter*, J. chem. Physics *21*, 836 (1953).

[14] *A. P. Marchetti & D. R. Kearns*, J. Amer. chem. Soc. *89*, 768 (1967).

[15] *F. Perrin*, C. r. hebd. Séances Acad. Sci. *178*, 1978 (1924); *S. I. Vavilov*, Ž. eksp. teor. Fiz. *13*, 13 (1943).

[16] *A. Dunant & R. Gerdil*, Helv. in preparation.

[17] *M. A. El-Sayed*, Nature *197*, 481 (1963); Accounts chem. Res. *4*, 23 (1971).

[18] a) *J. K. Roy & M. A. El-Sayed*, J. chem. Physics *40*, 3442 (1964); b) *K. B. Eisenthal*, ibid. *50*, 3120 (1969); c) *H. S. Judeikis & S. Siegel*, ibid. *53*, 3500 (1970); d) *A. Adamczyk & D. Phillips*, J. chem. Soc. Farad. Trans. II *70*, 537 (1974).

[19] *A. C. Albrecht*, J. mol. Spectroscopy *6*, 84 (1961).

[20] *W. Amrein & K. Schaffner*, Helv. *58*, 380 (1975).

[21] *L. F. Fieser & M. D. Gates*, J. Amer. chem. Soc. *62*, 2335 (1940).

[22] *J. S. Meek, F. M. Dewey & M. W. Hanna*, J. org. Chemistry *32*, 69 (1967).

[23] *C. S. Marvel & W. C. Hinman*, J. Amer. Soc. *76*, 5435 (1954).

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49. ^{1}H- and ^{13}C-NMR. Studies of the Molecular Conformations of Cyclo-Tetraglycyl [1]

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Summary. The ^{1}H- and ^{13}C-NMR. spectra of cyclo-tetraglycyl show that the four peptide groups are magnetically equivalent, and different from either a standard *trans* or a standard *cis* peptide group. It is suggested that the observed NMR. features correspond to a non-planar form of the peptide groups. On the one hand these data confirm the earlier conclusions from theoretical investigations of the molecular geometry, that cyclic tetrapeptides could not contain four standard *trans* peptide groups. On the other hand they are not consistent with a previously suggested alternative molecular conformation according to which cyclo-tetraglycyl would adopt a conformation similar to cyclo-tetrasarcosyl, with two *cis* and two *trans* peptide bonds. The different