(δ 3.98) showed $J_{4,6} \leq 0.5$ Hz. If the hydroxyl group were located at C(5) a larger coupling constant ($J_{4,5}$) would be expected.

The above assignments were verified by the successful ring closure of alcohol **7** to 3-oxawurtzitane (**8**). Hydroxymercuration of **7** with mercuric acetate in water, followed by $NaBH_4$-reduction in aqueous sodium hydroxide solution, gave **8** in 80% yield with respect to reacted starting material (60% isolated material). The intramolecular ether formation was also accomplished in lower yields with sulfuric acid in benzene or ether solutions. 3-Oxawurtzitane (**8**), m.p. 312–313° shows the following spectral properties: IR. (CCl_4): 1029; ^{1}H-NMR. ($CDCl_3$): 2.33/*m*, H–C(1) and –C(9); 4.24/*m*, H–C(2) and –C(4), $J_{1,2} = J_{4,9} = 10$ Hz (determined by double irradiation experiments); ^{13}C–NMR. ($CDCl_3$): only seven lines due to the symmetry plane through O(3), C(7) and C(10) δ 69.7 (2 C); 31.2 (2 C); 31.2 (2 C); 29.8 (2 C); 28.0 (1C); 27.8 (1 C); 24.2 (1 C).

Financial support for this research by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Ciba-Geigy AG*, Basel, is gratefully acknowledged.

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275. Selective Population of the n,π^* and π,π^* Triplet States of 1-Indanones

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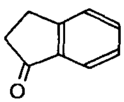
(11. X. 74)

Summary. The two components of the dual phosphorescence of 1-indanone (**1**) and six related ketones (**2–7**) possess different excitation spectra exhibiting the vibrational progression characteristic of the $S_0 \rightarrow S_1$ (n, π^*) transition (shorter-lived emission) and two bands of the $S_0 \rightarrow S_{2 \text{ and } 3}$ (π, π^*) 0–0 transitions, respectively. The most favorable intersystem crossing routes are S_1 (n, π^*) → T (n, π^*) and $S_{2,3}$ (π, π^*) → T (π, π^*). Internal conversion to S_1 competes more effectively with S (π, π^*) → T (π, π^*) intersystem crossing only from higher vibrational levels of the S_2 and S_3 states.

In the course of a stereochemical study of the intramolecular electronic energy transfer in bridged compounds with conformationally rigid orientations of 2,3-indanono and naphtho chromophores [1] we have investigated some of the luminescence properties of the hexahydrofluorenone **2** and the bridged analogues **3–7** in ether/isopentane/ethanol 5:5:2 (EPA) at 77K. Like the parent ketone 1-indanone (**1**) these six compounds do not fluoresce at room temperature owing to near-unity intersystem crossing yields, and at 77 K they exhibit a non-exponential luminescence decay attributable to simultaneous phosphorescence from two almost isoenergetic triplet states of different lifetimes. Since the discovery of this anomaly by *Yang & al.* [2] in a study of **1**, similar observations with other aromatic ketones have been reported [3–5] and controversial explanations for the case of indanone have been offered [2] [6–9]. The initial assignment of the two emissions to the n, π^* (shorter-lived emission) and π,π^* triplets (longer-lived) by *Yang* [2] finds strong support in recent work by *Lim & al.* [9] who advocate for a lack of sufficiently close-lying vibrational levels in the two energetically almost degenerate triplet configurations of **1** (in EPA) to account for their failure of rapid equilibration at 77 K. Other proposals – though perhaps not exhaustive – have been rejected on experimental grounds. Our own observations do not pertain directly to this problem (although they add further support to the configurational assignment to the phosphorescing states) but provide the first experimental evidence for a selective population of the two emitting triplet states in EPA at 77 K.

Contrary to a claim in [9] we find that the emissions of **1**, as well as **2**–**7**, possess distinctly different excitation spectra rather than one common excitation spectrum. In all cases either of the two phosphorescence and phosphorescence excitation spectra can be obtained in almost pure form when the appropriate conditions for excitation and emission are chosen (see Table and Fig. 1). The emission and excitation spectra of the seven ketones are practically indistinguishable from each other in their shape characteristics and the band positions vary only slightly. They are exemplified by an arbitrarily chosen set of spectra in Fig. 2 and 3. Irradiation in the 313–360 nm region within the $n \rightarrow \pi^*$ band with an open light path (shutter removed from the phosphoroscope) generates a phosphorescence with a preponderately *exponential* decay and a lifetime of 1.7–4.0 ms. The excitation spectrum of this short-lived emission exhibits the vibrational progression typical of the $n \rightarrow \pi^*$ transition, and it is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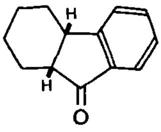
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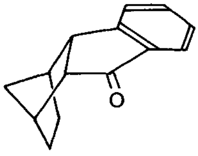
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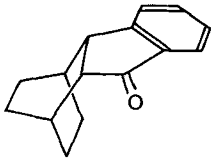
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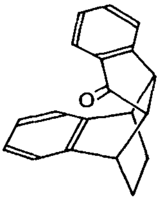
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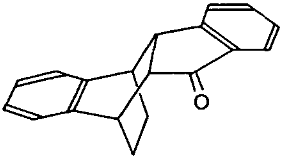
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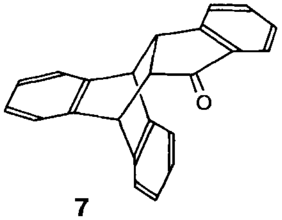
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Table. *Phosphorescence Data of Compounds* **1–7**

Ketone	Excitation (nm)	Phosphorescence O—O Band (nm)	E_T (kcal/mol)	τ_p (ms)	Φ_p (tot)
1	297a)	375	76.2	4.0	0.56 [2]
	302b)	378	75.6	270	
2	297a)	383	74.6	3.3	
	302b)	383	74.6	230	
3	297a)	389	73.5	1.9	0.50
	302b)	384	74.5	158	
4	297a)	384	74.5	1.7	0.60
	302b)	381	75.0	170	
5	297a)	381	75.0	2.3	0.45
	302b)	380	75.2	170	
6	297a)	381	75.0	1.8	0.45
	302b)	384	74.5	160	
7	297a)	382	74.8	2.4	
	302b)	383	74.6	155	

a) Measurement using phosphoroscope *with* light shutter (delay time *ca.* 7 ms).

b) Measurement using phosphoroscope with light shutter *removed* (open light path).

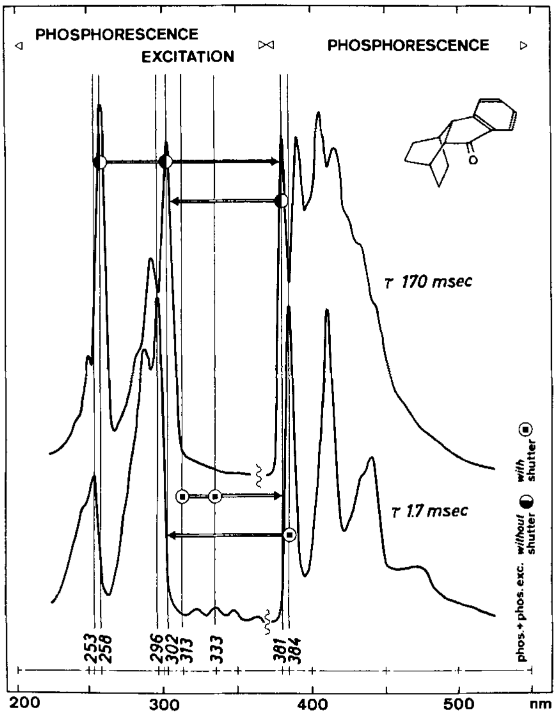

Fig. 1. *The two phosphorescence and phosphorescence excitation spectra of ketone* **4** *at optimum resolution* (in EPA at 77 K)

practically identical with the ketone absorption spectrum. Alternatively, the longer-lived phosphorescence (155–270 ms) shows an excitation spectrum with two very intense and sharp maxima at 258 and 302 nm characteristic of conjugative $\pi \rightarrow \pi^*$ absorption bands of the indanone system. This phosphorescence is predominantly produced upon irradiation at 258 and 302 nm through the light shutter providing for a delay time of 7 ms. An example of the two phosphorescence and phosphorescence excitation spectra at optimum resolution is given in Fig. 1. Apparently, the bands at 258 and 302 nm correspond to the 0–0 transitions of two π,π^* singlet states, and only excitation close to the zeroth vibrational level of these states provides for a selectivity in emission favoring the longer-lived component. Irradiation at other wavelengths in the $\pi \rightarrow \pi^*$ (*e.g.*, at 250 and 296 nm) and $n \rightarrow \pi^*$ absorption ranges (at 330 nm) reverses the selectivity and the shorter-lived phosphorescence previals. Fig. 2 and 3 give a comparison of the contribution of the longer-lived component to the total emission at each of these wavelengths.

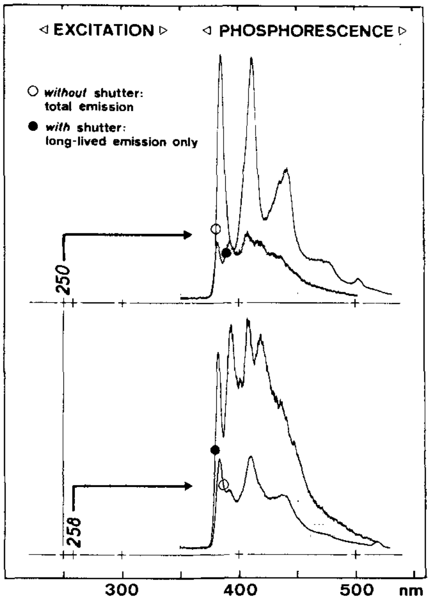

Fig. 2. *Composition of the dual phosphorescence of ketone* **4** *on excitation at 250 and 258 nm*[1])

These findings are compatible with the assignment of the emissions to thermally not rapidly equilibrating n, π^* and π,π^* triplets of the indanone system. They demonstrate, furthermore, that the intersystem crossing processes between the n,π^* singlet (S_1) and n,π^* triplet states as well as between the lowest vibrational levels of the π,π^* singlet (S_2 and S_3) and π,π^* triplet states are more probable than the alternative routes S_1 $(n,\pi^*) \rightarrow T$ (π,π^*) and $S_{2,3}$ $(\pi,\pi^*) \rightarrow T$ (n,π^*) which would

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[1]) The sensitivity ratio of the two curves (for total phosphorescence and longer-lived component) is the same for all excitation wavelengths in Fig. 2 and 3. *The percentage contribution of the longer-lived to the total emission, however, can be estimated only from the curve shapes.*

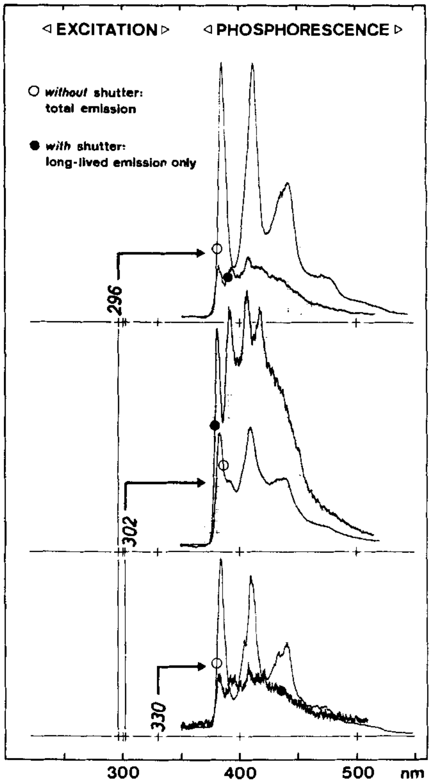

Fig. 3. *Composition of the dual phosphorescence of ketone* **4** *on excitation at 296, 302, and 330 nm*1)

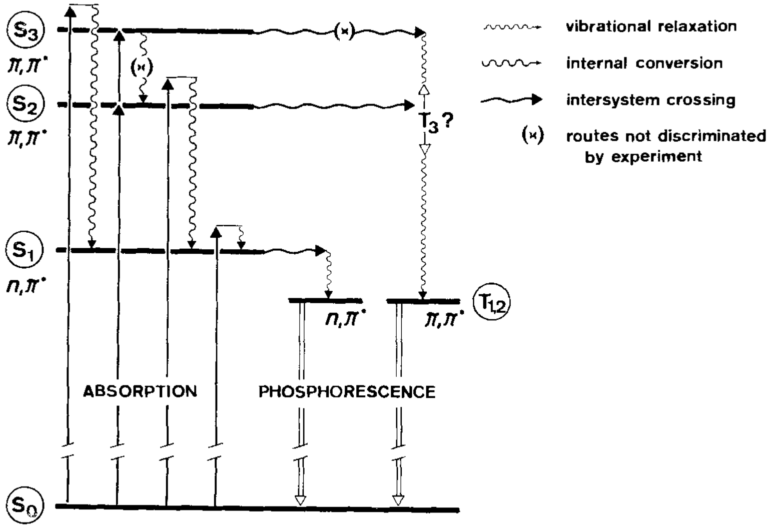

Fig. 4. *State diagram of indanone with the* preferred *internal conversions and intersystem crossing processes* (in EPA at 77 K)

follow the selection rules ascribed to spin-orbit interactions [10][2]. Internal conversion to the S_1 level begins to compete more effectively with S (π,π^*) → T (π,π^*) intersystem crossing only from higher vibrational levels of the S_2 and S_3 states, *i.e.*, such internal conversions proceed directly into the S_1 manifold prior to vibrational relaxation to the $^0S_2$ and $^0S_3$ levels. The hypothetical possibility exists that an upper π,π^* triplet state (T_3), which is energetically placed above S_1, may interpose on the route(s) from the S_3 and/or S_2 to the lowest T (π,π^*) state. This and other details, *e.g.* a discrimination between internal conversion to S_2 or direct intersystem crossing to the lowest-lying π,π^* triplet from S_3 in the absence of an energetically suitable triplet higher than S_2, are beyond the scope of this investigation.

Fig. 4 summarizes the conclusions concerning the radiationless processes which determine the spectral selectivities observed. The assumption is made here that the two phosphorescences have their origin in like molecules rather than in differently solvated species[3].

Financial support of this work by the *Fonds National Suisse de la Recherche Scientifique* and *Firmenich SA*, Geneva, is gratefully acknowledged. We also thank Professor *Pl. A. Plattner* for a generous financial contribution used for improvements of and complements to our spectroscopic instrumentation.

Experimental Part. – *Compounds.* Racemic forms of ketones **2**–**7** were used. 1-Indanone (**1**) was purchased in 'puriss.' quality from *Fluka* AG. *cis*-1,2,3,4,4a,9a-Hexahydrofluorenone (**2**) was synthesized by photocyclization of 1-benzoylcyclohexene; *cf.* [12]. *exo*-1,4-Methano-*cis*-1,2,3,4,4a,9a-hexahydro-fluorenone (**3**), 1,4-ethano-*cis*-1,2,3,4,4a,9a-hexahydro-fluorenone (**4**), and 1-oxo-6,11-*o*-benzeno-5b,6,11,11a-tetrahydro-indeno[3,2-*b*]naphthalene (**7**; *cf.* [13]), were obtained by cycloaddition of indenone to cyclopentadiene, 1,3-cyclohexadiene (and catalytic hydrogenation of the double bond in the adducts), and anthracene, respectively. The final step in the synthesis of *endo*- (**5**) and *exo*-1-oxo-6,11-ethano-5b,6,11,11a-tetrahydro-indeno[3,2-*b*]-naphthalene (**6**) involved $BF_3/SnCl_4$-catalyzed cyclization of 2-benzoyl-1,4-ethano-1,4-dihydronaphthalene. Full experimental details on **3**–**7** will be published in forthcoming work in other connections. Prior to use, the samples of **1**–**7** were crystallized to constant m.p. and their purity was checked by thin-layer chromatography, IR., MS., ^{1}H–NMR., and UV. spectra.

Spectroscopy. A modified *FICA* 55 spectrophotometer with a phosphoroscope designed in this laboratory (now commercially available from *Holzer Instrumentation Scientifique*, Lausanne) was employed. Light source XBO-450 W high-pressure Xe lamp; photomultiplier R 106; spectral resolution 2.5 nm; diameter of sample tube 2 mm. The mechanical construction of the phosphoroscope is similar to that described in [14]. The stepwise operation of the shutter cylinder is controled by an electronic quartz time base; invariable delay time between entrance and exit phase 7 ms; the shutter cylinder can be removed from the light path. – The *spectra* were run on one-channel operation mode at repetition intervals of 40 or 100 ms. – *Phosphorescence lifetimes* of $\tau \geqslant$ 10 ms were measured by external synchronization of the shutter with an oscilloscope, and for $0.5 \leqslant \tau \leqslant 10$ ms the shutter was removed and a chopper disk of 12000 rpm was used to modulate the excitation beam; time constant (mechanical shutting including electronic damping factor) $\leqslant 0.1$ ms. – For the determination of the *total quantum yields of phosphorescence* [Φ_P (tot)] the emission spectra were recorded linear in wavenumbers and intensity-corrected on two-channel (rhodamine B) operation mode. Solution of $T \geqslant 90\%$ at $d = 1$ mm and of similar extinctions

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[2] Note in this connection the proposal of a new selection rule by *Azumi* [11].

[3] This important point is supported by the observation that the long-lived emission is still observed, although with considerably weaker relative intensity, in hydrocarbon glasses (*cf.* [2]). In 3-methylpentane (77 K), $\Delta E_T(\pi,\pi^*\text{-}n,\pi^*)$ of **4** ~650 cm^{-1} (in EPA: ~200 cm^{-1}), $\tau_P = 1.4$ and 125 ms, and the intersystem crossing selectivities remain qualitatively as in EPA.

at the excitation wavelength (340 nm) were used. Spectral area integrations were corrected for the small variations in extinction. As a reference for Φ_p (tot) of **2**–**7** served the known value of benzophenone ($\Phi_p = 0.59$) [15]. The reproducibility of the measurements was better than ± 10%. Φ_p (tot) of **1** is known from the literature [2].

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276. Zur Reaktionsweise von Enaminen mit Cyclopropenonen V[1]). Einsatz von β-Carbonyl-enaminen

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(9. IX. 1974)

Summary. Diphenylcyclopropenone (**10**) was heated with five different β-carbonyl-enamines, namely 4-pyrrolidino-pent-3*E*-en-2-one (**12**), 4-dimethylamino-pent-3*E*-en-2-one (**13**), 4-dimethylamino-but-*E*-en-2-one (**14**), 3-dimethylamino-1-phenyl-prop-*E*-en-1-one (**15**) and ethyl 3-pyrrolidino-isocrotonate (**16**). The resulting reactions were more sluggish than those of **10** with ordinary enamines. The main reaction (between 10 and 69% yield) was in all cases a 'C, N-insertion'. The major products were: from **12**: an inseparable mixture of 4-methyl-6-oxo-2,3-diphenyl-hepta-2*E*,4*E*-dienoic acid pyrrolidide (**17**) and its 2*Z*,4*E*-stereomer (**18**); from **13**: 4-methyl-6-oxo-2,3-diphenyl-hepta-2*E*,4*E*-dienoic acid dimethylamide (**19**) and its 2*Z*,4*E*-stereomer (**20**); from **14**: 6-oxo-2,3-diphenyl-hepta-2*E*,4*E*-dienoic acid dimethylamide (**21**); from **15**: 6-oxo-2,3,6-triphenyl-hexa-2*E*,4*E*-dienoic acid dimethylamide (**22**); and from **16**: 5-ethoxycarbonyl-4-methyl-2,3-diphenyl-penta-2*E*,4*E*-dienoic acid pyrrolidide (**23**) and its 2*Z*,4*E*-stereomer (**24**). The constitutions of **17** to **24** were derived mainly from spectral properties.

For these products the *E*-configuration at the 4,5-double bond was assigned on the assumption that the insertion of the side-chain (cyclopropenone carbons) between the enamine carbon and nitrogen atoms occurred with retention of configuration, as had been concluded earlier. This was confirmed in the cases of **21** and **22** by the *trans*-coupling between H—C(4) and H—C(5) in the ^{1}H—NMR. spectrum, the educts (**14** and **15**) having the *E*-configuration. The configurational difference between the stereomeric products **17**/**18**, **19**/**20** and **23**/**24** was, therefore

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[1]) Aus der geplanten Dissertation von *Vanda Bilinski*, Universität Zürich.