The synthesis of cyclodecasarcosyl has not been reported before. The *N*-protected decapeptide was obtained by coupling two pentapeptides, using the same general methods as already described,[6] and the trichlorophenyl ester cyclized in pyridine, yield 50 %, m.p. 280 – 282 °C.

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On the Fluorescence of Propellicene

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Certain crowded polyaromatic molecules, most notably 9,9′-bianthracene,[1,2] exhibit a surprising charge-transfer emission in many solvents. Although the theory of the emission has not been worked out in detail, the observation of a charge-transfer emission may be ascribed to (a) fluctuations in the solvent arrangements within a sufficiently polar solvent environment which permit the evolution of a cybotactic region[3] that stabilizes a charge-transfer state and (b) lack of rapid quenching pathways for nonradiative decay of the charge-transfer state. In 9,9′-bianthracene, a perpendicular relationship of the two rings leads to decay rates of the charge-transfer state which are lower than the radiative rate.[4] It was thus of interest to find whether the unusual cyclic helicene, propellicene (see Fig. 1; the formula),[5] could give rise to charge-transfer emissions.

Fluorescence spectra were measured in dioxane and dioxane-water mixtures, and in glycerol. The insolubility of propellicene in glycerol forced us to examine a dispersion of a dioxane solution of the compound in glycerol. The fluorescence lifetimes and quantum yields of fluorescence were also measured in dioxane and 33 % dioxane-water solutions.

In no case was a charge-transfer emission observed. The fluorescence quantum yield is not particularly high, but the quenching mechanisms were not further investigated. A structured fluorescence spectrum with peaks at 413 and 433 nm (shoulders at 463 and 495 nm) can be observed in dioxane. Addition of water does not affect the emission spectrum until a composition of 33 % dioxane-water is reached, at which point, the spectrum shifts to 10 nm longer wavelengths without change in excitation spectrum. The excitation spectrum in all cases was identical with the absorption spectrum.

Lifetime data and derived rate constants are shown in Table 1. The fluorescence lifetimes of helicenes are extremely long[6] and propellicene is no exception. The absorption and fluorescence spectra of propellicene resemble those of hexahelicene.[6]

The change in position of the fluorescence maxima in 33 % dioxane-water from those found for pure dioxane is probably due to an aggregate (dimer?) of propellicene. The spec-

Table 1. Fluorescence lifetimes, quantum yields and derived rate constants for propellicene.

	Dioxane-water mixtures Vol. % dioxane 100	33.3
$E_T(30)$ [a]	36.0	56.5
Φ_F [b]	0.034	0.012
τ_{obs}/ns	12.2	3.58
$k_r/10^7\ s^{-1}$ [c]	0.279	0.235
τ_r/ns	358	293
$k_{nr}/10^7\ s^{-1}$ [d]	7.93	27.6

[a] Solvent polarity parameter, see Ref. 8. [b] Quantum yield of fluorescence. [c] Radiative rate constant, $k_r = \Phi_F/\tau_{obs}$. [d] Nonradiative rate constant, $k_{nr} = (1 - \Phi_F)/\tau_{obs}$.

trum in dioxane dispersed in glycerol resembled that in dioxane.

The lack of a charge-transfer emission probably implies that the nonradiative rate for a charge-transfer state is too high. Overlap between the positive and negative ends of a charge-transfer state are apparently too great to allow the separated charges to be stabilized by solvent traps. Appropriately substituted propellicenes (with donor and acceptor groups at opposite ends of the molecule; appropriately substituted helicenes might also serve the purpose) might give rise to charge-transfer emissions.

Experimental. Propellicene was available from a previous synthesis.[5] UV spectra were measured with a Cary model 17 recording spectrometer. Fluorescence spectra (corrected) (temperature controlled at 25.0 °C) were recorded with a Hitachi-Perkin-Elmer MPF-4 with a corrected spectra attachment. Fluorescence lifetimes were measured by the single photon counting technique with a setup similar to that described by Berson and Horowitz.[7] Dioxane was Spectrograde and glycerol was for fluorescence microscopy (E. Merck and Co., Darmstadt).

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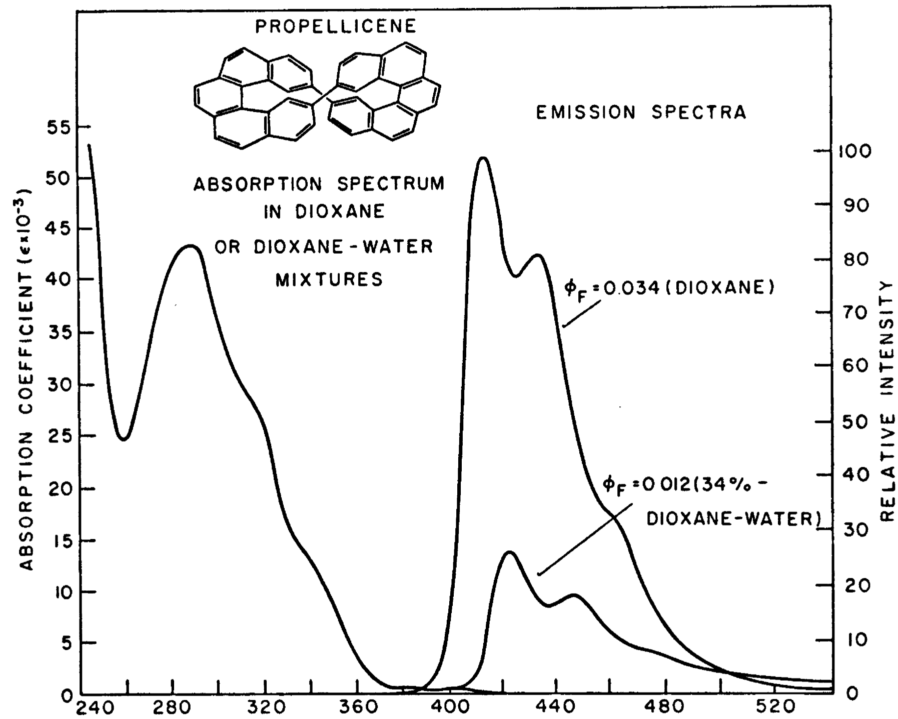

Fig 1. Absorption spectrum and emission spectra for propellicene.

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Mass Spectral Differentiation of Some Unsymmetrically Substituted Isomeric Dihydrobarbiturates

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Recently it has been shown that the sodium borohydride reduction of some unsymmetrically substituted barbituric acid derivatives such as 1-methyl-5-ethyl-5-phenylbarbituric acid (MEPBA, *1*) leads to the formation of two different dihydrobarbiturates.[1] From a mass spectral investigation of the products formed it was found that mass spectrometry provides a method by which they can be easily distinguished. In the present communication we describe the results mainly obtained using the dihydrobarbiturates *2* and *3*, derived from *1*.

The mass spectral fragmentation of unreduced barbituric acid derivatives is well-known and it has been shown that the preferential fragmentation is strongly influenced by the nature of the C-5 substituents.[2–4] See also Refs. 5–11.

Fig. 1 shows the mass spectrum of 1-methyl-5-ethyl-5-phenyl-6-dihydrobarbiturate *2*. The fragmentation is strongly dominated by the formation of an abundant ion corresponding to *m/e* 146 (base peak). Its formation and further fragmentation are depicted in Scheme 1. The loss of water from the molecular ion has also taken place to a certain extent.

Fig. 2 shows the mass spectrum of 1-methyl-5-ethyl-5-phenyl-4-dihydrobarbiturate *3*. The formation of the base peak at *m/e* 146 can be depicted in a manner analogous to the previous case (Scheme 2, Route A). The elimination of water leads to the ion of *m/e* 230* which may fragment to the ion of *m/e* 146. However, its main fragmentation path is of *retro*-Diels-Alder type, leading to an abundant ion of *m/e* 173. Its formation and further fragmentation are depicted in Scheme 2 (Route B).

It is worthy of note that the McLafferty rearrangement of the C-5 ethyl substituent, dominating the mass spectral fragmentation of similar unreduced barbituric acid derivatives (*e.g.* 5-ethyl-5-phenylbarbituric acid, Luminal® *4*),[3] is not present in any appreciable amount in either case.

The importance of the *retro*-Diels-Alder process in the mass spectral behaviour of *3*, in all probability due to the vicinity of the OH- and NH-groups permitting the thermal 1,2-elimination of water (*vide supra*), can be used successfully to differentiate between *2* and *3*. In an analogous manner, the peaks at *m/e* 159 and *m/e* 149 in the mass spectra of *6* and *8*, respectively, permit the differentiation of *6* and *8*

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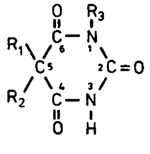
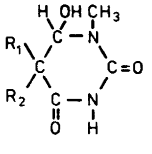
* The peak at *m/e* 230 (*vide supra*) is, in all evidence, due mainly to the molecular ion of the olefin produced by thermal loss of water prior to ionization.



1. $R_1 = C_6H_5$; $R_2 = C_2H_5$; $R_3 = CH_3$

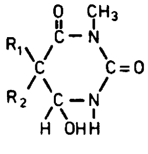
4. $R_1 = C_6H_5$; $R_2 = C_2H_5$; $R_3 = H$



2. $R_1 = C_6H_5$; $R_2 = C_2H_5$

5. $R_1 = C_6H_5$; $R_2 = CH_3$

7. $R_1 = R_2 = CH_2{=}CH{-}CH_2$



3. $R_1 = C_6H_5$; $R_2 = C_2H_5$

6. $R_1 = C_6H_5$; $R_2 = CH_3$

8 $R_1 = R_2 = CH_2{=}CH{-}CH_2$