

The Triplet States of Morphine and Diamorphine

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Summary The weak phosphorescence emission from the triplet state of diamorphine (heroin) in ethanol at 77 K has been located, and differs significantly from that of the parent morphine.

THE characteristics of the singlet and triplet states of morphine and diamorphine (heroin) are not fully known. The phosphorescent triplet state of diamorphine, in particular, has not hitherto been located. We now present precise measurements of the emission spectra of these molecules.

Excitation of morphine in ethanolic solution at 25 °C results in a weak fluorescence emission at 340 nm, with a quantum yield of 0.030. Fluorescence decay-time measurements using a time correlated single photon counting technique show a fluorescence lifetime of 0.7 ± 0.1 ns. At 77K the fluorescence maximum moves to shorter wavelength (328 nm) due to emission from the Franck-Condon state, and a broad structureless phosphorescence emission

is observed in the 400–650 nm region with maximum at 522 nm, and a lifetime of 0.020 s.

Diamorphine affords significantly different emission spectra. The fluorescence emission in ethanol at 25 °C appears at shorter wavelength (312 nm) with a lower quantum yield ($\phi_f = 0.0025$). Because of the very low value of ϕ_f , it was not possible to determine the fluorescence decay time with the present instrumentation. At 77 K the fluorescence maximum moves to 305 nm, and an extremely weak phosphorescence emission is observed in the region 350–600 nm with the maximum at 445 nm. The ratio of the phosphorescence intensities of morphine and diamorphine is approximately 10:1.

The spectroscopic equipment used in this investigation has been described earlier.¹ All emission spectra are corrected for instrumental response using a quantum counter technique.²

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¹ A. Bowd and J. H. Turnbull, *J.C.S. Perkin II*, 1973, 1312.

² W. H. Melhuish, *J. Opt. Soc. Amer.*, 1962, 52, 1256.