

Spectra & Conformation of α -Furil

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The absorption spectrum of α -furil changes from 410 to 490 nm by changing the environment from solution to crystalline phase, and the green emission appearing at 530 nm in solution changes to yellow emission appearing at 560 nm in the crystal. This has been explained by assigning a planar molecular conformation in the crystalline state, although it is known to exist in puckered form in solution.

The aromatic α -dicarbonyls like benzil¹⁻⁵, ortho-tolil⁶, naphthils^{7,8} etc. show puckered to planar conformation change either in ground or in excited electronic state. This is perhaps mainly due to the small π -bond character around central CO-CO bond as revealed by its bond length^{9,10} of 1.52 Å and calculated π -bond order¹¹ of 0.2. An exception to the above mentioned α -dicarbonyls is the α -pyridil¹² which does not show the conformation change on photoexcitation. Hence it is interesting to find out the various

environmental conditions and molecular properties which are responsible for such conformation change. In this context, we have made the spectral studies on α -furil and the results are presented in this note.

α -Furil was prepared¹³ from furfural (BDH) and recrystallised from benzene. Large yellow crystals were grown from methanol by slow evaporation. Solvents were purified by standard procedures. Spectral studies were made with Cary 17D spectrophotometer and MPF 44B Perkin-Elmer fluorimeter. The phosphorescence life times were measured by EC storage oscilloscope (OS 768S) using Moletron N₂ laser (UV 1000).

The solution spectra of α -furil are shown in Fig. 1 (curves a-c). The room temperature absorption spectrum of the compound in methylcyclohexane (Fig. 1a) shows the band maximum at 425 nm. It is blue shifted (Fig. 1a') and is less prominent in ethanol (an usual characteristic of $n\pi^*$ band). However at 77 K in ethanol glass it shows a prominent peak at 410 nm (Fig. 1b) and green phosphorescence of life-time 4.5 ms with maximum at 520 nm (Fig. 1e). The excitation spectrum (Fig. 1d) monitoring 530 nm or 570 nm emission band corresponds to the absorption

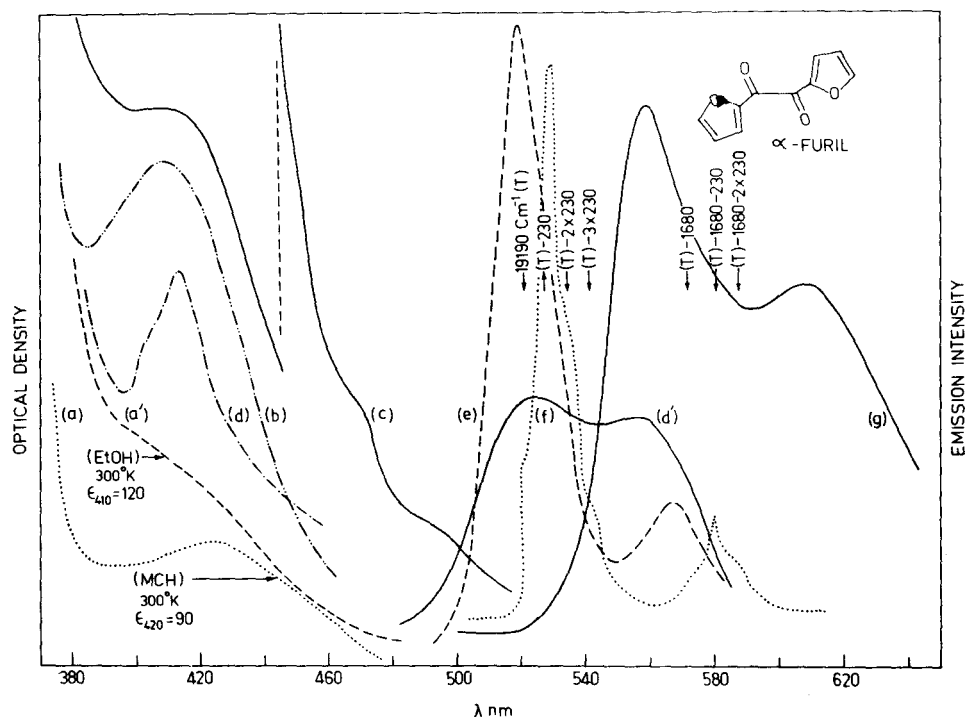


Fig. 1—Absorption spectra of α -furil at 300 K [(a) in methylcyclohexane; (a') in ethanol; (b) at 77 K in ethanol; and (c) in solid state (crystal) at 77 K. Emission spectra of α -furil at 77 K [(e) in ethanol glass; (f) in *n*-octane matrix; and (g) in solid state (crystal)] Excitation spectra of α -furil at 77 K [(d) in ethanol monitoring 520 nm emission; and (d') in solid state (crystal) monitoring 610 nm emission band]

spectrum. The emission spectrum in *n*-octane matrix (Fig. 1f) shows better resolution and progressions of two frequencies 1680 and 230 cm^{-1} . The former could be identified as $\nu\text{C}=\text{O}$ and the latter is likely a low frequency torsional mode around $\text{CO}-\text{CO}$ bond.

The absorption, emission and excitation spectra of α -fural crystal are shown in Fig. 1 (curves c, g and d' as solid curves). There are two prominent humps located around 490 and 470 nm on the strong rising absorption at the shorter wavelength region. The crystal shows yellow emission (green emission in ethanol glass) with two prominent bands at 560 and 610 nm (Fig. 1g). The emission from α -fural crystal has a life-time of 8.5 ms at 77 K. The excitation spectrum recorded by monitoring 610 nm band shows bands at 525 and 550 nm (Fig. 1d').

The molecular conformation of α -fural is puckered¹⁴ in solution as determined from dipolemoment measurements. The angle between planes containing two halves has been estimated to be 118.5° . The absorption spectrum in solution and emission spectrum in glassy matrix of α -fural are similar to those of other puckered dicarbonyls under similar conditions. The large red shift of $n\pi^*$ bands could not be explained due to matrix effect and have not been noticed in crystals of other puckered dicarbonyls. On the other hand, planar benzil (benzil doped in *trans*-stilbene^{1,2} and methylcyclohexane matrices³), other planar benzil derivatives¹⁶ and mesitol¹⁵ (2,2',4,4,6,6'-hexamethylbenzil) show absorption around 490 nm close to that of α -fural crystal. The *trans* planar moiety in mesitol has been confirmed by X-ray structure analysis¹⁷. The yellow emission at 560 nm in α -fural crystal is also very much similar and close to the emission of photoexcited planar benzils⁴⁻⁶ and mesitol¹⁵. The excitation spectrum recorded by monitoring emission at 610 nm shows bands at 555 and 525 nm. The 555 nm band is close to 560 nm emission band indicating that the excitation bands are of singlet-triplet origin. From these spectral similarities with planar dicarbonyls, the *trans* planarity of $\text{CO}-\text{CO}$ group in α -fural crystal could be inferred. We have studied the IR spectra of α -fural in solution and

crystalline state. There is no perceptible change in νCO mode. Perhaps the angle of 118.5° between planes containing halves of the molecule in solution¹⁴ is already too wide for νCO mode to be sensitive for further widening of the interplanar angle. The low frequency twisting or torsional mode which appears in the emission from *n*-octane matrix (Fig. 1f) might be sensitive to such conformation change. The lack of facilities forbid us to study in this low frequency region. Unlike other dicarbonyls, α -fural does not show any photorotamerism. The emission of α -fural at 520 nm remains unchanged on melting the glassy matrix, even at room temperature. This is in contrast to other dicarbonyls except α -pyridil. Hence α -fural shows similar rigidity to photorotamerism as found in case of α -pyridil.

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