

Short Communication

Do aromatic C-nitroso compounds fluoresce from their second excited singlet states?

D. A. CONDIRSTON, A. R. KNIGHT and R. P. STEER

Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan S7N 0W0 (Canada)

(Received July 18, 1980)

1. Introduction

Molecules which are known to fluoresce strongly and/or to react chemically from excited singlet states higher in energy than S_1 are relatively small in number but have evoked sustained interest in recent years [1, 2]. The "anomalous" $S_2 \rightarrow S_0$ fluorescence of azulene and several other non-alternant hydrocarbons has been studied for nearly 30 years [3 - 5]. More recently, both the chemical reactions and the photophysical decay processes of thiocarbonyls in their $S_2[{}^1(\pi, \pi^*)]$ states have received considerable attention [1, 6 - 8]. Such molecules are of importance since strongly fluorescent and highly excited electronic states make possible pump-probe measurements of the dynamics of the decay of lower excited states. It is therefore of interest to seek other classes of compounds which may fluoresce strongly from electronic states higher than S_1 .

The aliphatic and aromatic C-nitroso compounds exhibit S_2 - S_1 electronic energy gaps which are comparable in magnitude with those of the thiocarbonyls and azulene [9]. Conflicting reports have appeared recently concerning the observation of $S_2 \rightarrow S_0$ fluorescence in two aromatic C-nitroso compounds, *i.e.* in nitrosobenzene and *p*-dimethylaminonitrosobenzene. Bhujle [10] failed to detect any emission which could be attributed safely to the S_2 state of nitrosobenzene either in the vapour phase or in various solvents at temperatures down to that of liquid helium. These observations have been confirmed very recently by Chernoff and Hochstrasser [11] who estimated that $\phi_f(S_2 \rightarrow S_0)$ was less than about 5×10^{-7} for nitrosobenzene vapour and less than about 1×10^{-5} for its *n*-heptane solution at 25 °C. Very weak emission, the spectrum of which was a reasonable mirror image of the $S_2 \leftarrow S_0$ absorption spectrum, was observed by Bhujle in room temperature solutions of *p*-dimethylaminonitrosobenzene. At 77 K in methylcyclohexane more intense structured emission was observed, but this proved to have an intensity which was exposure dependent and which could not be assigned with certainty to $S_2 \rightarrow S_0$ fluorescence from the parent molecule. Bunce [12], in contrast, reported that both nitrosobenzene and *p*-dimethylamino-

nitrosobenzene in solution at room temperature fluoresced from S_2 , using the mirror symmetries of their fluorescence and $S_2 \leftarrow S_0$ absorption spectra as a basis for the assignment. Two aromatic *N*-nitrosoaminobenzene compounds did not fluoresce.

2. Experimental

Emission and emission excitation spectra of nitrosobenzene, *p*-dimethylaminonitrosobenzene and *p*-diethylaminonitrosobenzene in hydrocarbon and ethanol solvents were measured at room temperature using a single-photon counting fluorescence spectrometer described previously [13]. Absorption spectra were recorded on a Cary 118 spectrophotometer.

Nitrosobenzene (Aldrich Chemical Co.) was purified by vacuum sublimation from 23 to -78°C and was free from detectable electron paramagnetic resonance signals. *p*-Dimethylaminonitrosobenzene (Aldrich) (melting point, $84 - 85^\circ\text{C}$) was recrystallized twice from 60 - 80 petroleum ether. *p*-Diethylaminonitrosobenzene (Aldrich) (melting point, $83 - 84.5^\circ\text{C}$) was recrystallized first from ligroin and then from 60 - 80 petroleum ether. Cyclohexane, 3-methylpentane and absolute ethanol were purified by standard techniques. The nitrosobenzenes exhibited absorption spectra identical with those reported in the literature [14].

3. Results and discussion

Emission spectra of sublimed samples of nitrosobenzene in carefully degassed cyclohexane solutions, excited at various wavelengths in the first strong absorption system ($S_2 \leftarrow S_0$, 340 - 280 nm), revealed features similar to those reported by Chernoff and Hochstrasser [11], *i.e.* a solvent Raman band Stokes shifted by approximately 2900 cm^{-1} from the exciting line and a very weak structureless emission peaking at 345 nm. The emission excitation spectrum, observed at 350 nm with low resolution, bears no resemblance to the absorption spectrum of nitrosobenzene in the range 330 - 260 nm. Indeed, the excitation peaks observed at 295 and 235 nm may indicate the presence of an aniline-like impurity. Similar spectra were obtained in air-saturated ethanol solution. We therefore agree with Chernoff and Hochstrasser and with Bhujle that nitrosobenzene excited to its second singlet state does not yield detectable fluorescence.

Experiments with *p*-dimethylaminonitrosobenzene and *p*-diethylaminonitrosobenzene yielded similar results. The absorption, emission and emission excitation spectra of these compounds in hydrocarbon solution indicate that the emission does not originate from the second excited singlet state. As an example, consider the spectra of *p*-diethylaminonitrosobenzene in 3-methylpentane shown in Fig. 1. It can be seen that the emission spectrum, which peaks at about 427 nm, bears a fair mirror symmetry relationship to the absorption spectrum. However, this fact alone cannot be the basis for assigning a particular electronic state as the emitting state. The fluorescence excitation spectrum should also bear some resemblance to the absorption spectrum, particularly at the long-wavelength end, and it is clear

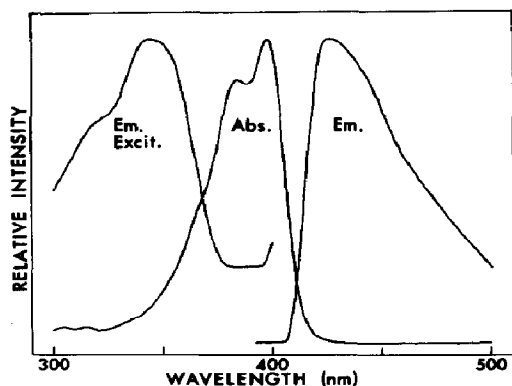


Fig. 1. Absorption, emission and emission excitation spectra of *p*-diethylaminonitrosobenzene in 3-methylpentane at 23 °C. Concentrations are 4×10^{-5} M for the absorption spectrum and 2×10^{-4} M for the emission and emission excitation spectra.

from Fig. 1 that this is not the case. Whereas the absorption spectrum shows two peaks, at 398 and 384 nm, the excitation spectrum has a broad maximum at 344 nm with essentially no intensity in the region of absorption. The intensity in the excitation spectrum might be due to *N,N*-diethyl-*p*-nitroaniline. Evidence of traces of this impurity was found in the mass spectrum of the purified nitroso compound, and its absorption spectra [15, 16] exhibit maxima near the observed maxima in the emission excitation spectra.

In degassed ethanol solution the emission maximum for each *N,N*-dialkyl derivative is red shifted to approximately 485 nm. The excitation spectra are more complex than those in hydrocarbon solution and they exhibit intensity over a wider spectral range, including the wavelengths at which these molecules have their $S_2 \leftarrow S_0$ absorption bands. The most distinct features of these spectra are a broad peak centred at about 395 nm and a stronger band located between 460 and 470 nm. Neither of these peaks, however, corresponds to the $S_2 \leftarrow S_0$ absorption maxima in either compound. It seems likely that in ethanol, as in hydrocarbon, impurities are responsible for the observed emission. We conclude that fluorescence of significant intensity does not occur from the second excited singlet state of either nitrosobenzene or its *p*-dimethylamino or *p*-diethylamino derivatives.

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for its continued financial support. We also wish to thank Dr. L. Mihichuk for taking electron paramagnetic resonance spectra of the nitrosobenzene samples.

1 P. de Mayo, *Acc. Chem. Res.*, **9** (1976) 52.

2 N. J. Turro, V. Ramamurthy, W. Cherry and W. Farneth, *Chem. Rev.*, **78** (1978) 125.

3 M. Beer and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23** (1955) 1390.

- 4 J. Sidman and D. S. McClure, *J. Chem. Phys.*, **24** (1956) 757.
- 5 G. Viswanath and M. Kasha, *J. Chem. Phys.*, **24** (1956) 574.
- 6 R. W. Anderson, Jr., R. M. Hochstrasser and H. J. Pownall, *Chem. Phys. Lett.*, **43** (1974) 224.
- 7 D. J. Clouthier, A. R. Knight, R. P. Steer and P. A. Hackett, *J. Chem. Phys.*, **71** (1979) 5022.
- 8 D. J. Clouthier, A. R. Knight, R. P. Steer and P. A. Hackett, *Chem. Phys. Lett.*, **70** (1980) 89.
- 9 V. Bhujle, U. P. Wild, H. Baumann and G. Wagniere, *Tetrahedron*, **32** (1976) 467.
- 10 V. U. Bhujle, *Spectrosc. Lett.*, **10** (1977) 587.
- 11 D. A. Chernoff and R. M. Hochstrasser, *Chem. Phys. Lett.*, **70** (1980) 213.
- 12 N. J. Bunce, *Chem. Phys. Lett.*, **59** (1978) 66.
- 13 T. Oka, A. R. Knight and R. P. Steer, *J. Chem. Phys.*, **63** (1975) 2414.
- 14 K. Tabei and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **38** (1965) 965.
- 15 O. S. Khalil and S. P. McGlynn, *J. Lumin.*, **11** (1975/76) 185.
- 16 T. Yokoyama, *Aust. J. Chem.*, **29** (1976) 1469.