Rotational Isomerism and Dual Luminescence in Dipolar Dialkylamino-Compounds

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Summary The feasibility of a rotational isomerisation model in accounting for dual luminescence of *p*-dimethylaminobenzonitrile and related compounds is substantiated by PPP–SCF–MO–CI calculations.

THE dual fluorescence of *p*-dimethylaminobenzonitrile (DABN) has aroused much controversy[1] concerning the emitting states, and has been ascribed to a solvent-induced inversion of electronic states, to a stepwise formation of excited complexes with solvent molecules, to protonation of excited species, to excimers, and to isomerisation of the excited molecule *via* internal rotation of the NMe_2 group.

The latter rotational isomerisation model advocated by Grabowski and his co-workers[2] has been discounted on the basis of a CNDO/s–CI calculation by McGlynn.[3]

We report, qualitatively the results of PPP–SCF–MO–CI calculations on DABN and related compounds. The computer program and parametrisation were conventional. Rotation about the ring C(1)–NMe_2 bond was represented by a variation of the resonance integral, β_{CN}, in the range 0 (90° twist) to $-2{\cdot}50$ eV (coplanar). The two-centre repulsion integral, γ_{CN}, was taken to be 5·4 eV for all rotation angles. For the coplanar isomer of DABN we obtain results in close agreement with those obtained by the CNDO/s method. However, in the twisted isomer the 2^1A_1 (^1L_a) state drops markedly in energy when $-\beta$ is less than *ca.* 1·5 eV, reaching 3·0 eV for $\beta = 0{\cdot}00$ eV, and its character becomes increasingly dominated by excitation from the amino nitrogen lone-pair.† Whilst CI accentuates the stabilisation of the excited twisted isomer it is not the sole effect. Examination of the component energy terms reveals that the change of the repulsion term γ_{CN}-$C_N(m)^2C_{LVMO}{}^2$ with twist about the C(1)–NMe_2 bond dominates all others [where C_N is the amino-nitrogen coefficient in the occupied MO '*m*', and C_{LVMO} is the coefficient of the ring carbon C(1) for the lowest vacant MO corresponding to the dominant configuration, LVMO $\leftarrow$ *m*, in the excited-state description]. This repulsion term only changes appreciably when, on twist about the C(1)–NMe_2 bond, the orbital '*m*' transforms from a delocalised MO to an isolated 2*p* orbital on the donor NMe_2.

This analysis can be extended to other systems of the type D–Ar–A where D is an electron-donor group distinguishable by rotation and A is an electron-acceptor group.

We predict that when D is of much higher ionisation potential than NMe_2 (*e.g.* when it is OMe), rotation about D–Ar does not lower the energy of any electronic state significant in luminescence. For strong π electron acceptor groups, *e.g.* A = NO_2, CH=CHNO_2, or 3,5-dichlorotriazinyl, rotation of the donor NMe_2 group does not lead to a lowering in energy of the charge-transfer state for in these cases C_{LVMO} is too small.

It appears that, for D = NMe_2, rotational isomerisation is feasible as an explanation of dual luminescence when A is C≡N or C(=O)X (X = H, alkyl, OH, or O–alkyl) in a *para* but not in a *meta* position with respect to the donor D. We predict that *para*-, but not *meta*-, *NN*-dimethylaminopyridine could exhibit dual luminescence.

These predictions are confirmed satisfactorily by further experimental data which we are accumulating. Dual luminescence is observed at room temperature for acetonitrile solutions of *p*-dimethylaminobenzaldehyde (380 and 530 nm), *p*-dimethylaminobenzoic acid (346 and 480 nm), and the methyl *p*-dimethylaminobenzoate (343 and 480) whilst a single fluorescence band only is observed for *m*-dimethylaminobenzoic acid (435 nm), (*p*-diethylaminophenyl)dichloro-1,3,5-triazine (420 nm), and *trans*-1-(4-*NN*-dimethylaminophenyl)-2-nitroethylene (520 nm).

It could be argued that both PPP and CNDO/s methods are unreliable in this area. Whilst this suggests that the results should be treated with caution, the success in correlation and usefulness as a stimulus for further experimental work justifies attention to the PPP results. The rotational isomerisation model is confirmed as feasible in a restricted area. The role of solvent polarity and other influences must, of course, be included in any detailed explanations of dual luminescence phenomena.

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† The π^* orbital is not the in-plane π^* orbital of the nitrile group suggested in ref. 2, but embraces the usual set of 2p AOs. In the 90°-twisted form the excitation is equivalent to $\pi^* \leftarrow n$.

[1] E. M. Kosower and H. Dodiuk, *J. Amer. Chem. Soc.*, 1976, **98**, 924, and references cited therein.

[2] K. Rotkiewicz, K.-H. Grellman, and Z. R. Grabowski, *Chem Phys. Letters*, 1973, **19**, 315; K. Rotkiewicz, Z. R. Grabowski, A. Krówczyński, and W. Kühnle, *J. Luminescence*, 1976, **12/13**, 877.

[3] O. S. Khalil, J. L. Meeks, and S. P. McGlynn, *Chem. Phys. Letters*, 1976, **39**, 457.