Electron Spin Resonance of the Triplet State of Some Aromatic Carbonyl Compounds

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Summary The e.s.r. spectra of some carbonyl derivatives of naphthalene which possess lowest triplet states of the π,π^* type, exhibit triplet state signals from which the zero-field-splitting parameters D and E can be calculated.

THE lowest triplet state of aromatic carbonyl compounds can be either n, π^* or π,π^* in character, or in certain cases, charge-transfer in character.[1,2] The majority of aromatic carbonyls possess lowest triplet states of the n, π^* type, and the e.s.r. spectra of the triplet state of these compounds have not been observed on account of the short phosphorescence lifetimes ($<0{\cdot}1$ sec.) of these states. Studies related to the photochemistry of aromatic carbonyl compounds have revealed that a number of aromatic carbonyl compounds possess lowest triplet states of the π,π^* type and that the phosphorescence lifetimes of these states can be relatively long.[1,3] Naphthalene-2-carbaldehyde, methyl 2-naphthyl ketone, and 2-naphthyl phenyl ketone possess lowest triplet states of the π, π^* type,[4] and we now report that the e.s.r. spectra of the triplet states of these compounds can be observed.

The spectra of u.v.-irradiated samples of naphthalene-2-carbaldehyde, methyl 2-naphthyl ketone, and 2-naphthyl phenyl ketone in EPA (ether–isopentane–ethanol) glass at 77°K exhibit typical triplet-state signals with a relatively intense "$\Delta m = 2$" transition and weak "$\Delta m = 1$" transitions. In contrast to the spectra of carbonyl derivatives of benzenoid compounds, where only the "$\Delta m = 2$" transition can be observed,[5] the spectra of the compounds studied herein show four of the six "$\Delta m = 1$" transitions. Analysis

of the spectra gave the parameters for the spin–spin interaction listed in the Table.

E.s.r. parameters for the triplet states of some derivatives of naphthalene

Compound	D	E	$(D^2 + 3E^2)^{\frac{1}{2}}$	D^*
Naphthalene-2-carbaldehyde	0·094	0·029	0·106	0·012
Methyl 2-naphthyl ketone	0·096	0·027	0·107	0·105
2-Naphthyl phenyl ketone	0·095	0·026	0·105	0·105
[$^2H_8$]Naphthalene†	0·100	0·015	0·103	0·101

† E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1763.

The values of the composite term D^* calculated from the position of the "$\Delta m = 2$" transition[6] are in agreement with the values for the equivalent term $(D^2 + 3E^2)^{\frac{1}{2}}$ calculated from the positions of the "$\Delta m = 1$" transitions. It can be seen from the Table that the values of D for the carbonyl derivatives of naphthalene are less than that for [$^2H_8$]naphthalene whilst the corresponding values of E are greater. The smaller values of D for the carbonyl derivatives of naphthalene as compared to the value for [$^2H_8$]naphthalene reflect the extended conjugation and the lower degree of interaction between the unpaired electron spins in the former compounds. The higher values of E are a measure of the lower symmetry of the carbonyl compounds.

Since aromatic carbonyl compounds possessing lowest triplet states of the π,π^* type can exhibit triplet-state signals whereas those with lowest triplet states of the n, π^* type do not, the e.s.r. technique may be used in certain cases to characterise lowest triplet states. However, the absence of a triplet-state signal does not necessarily mean that the lowest triplet state of the carbonyl compound is of the n, π^* type since the phosphorescence lifetimes of π,π^* states can be too short to allow detection.

The e.s.r. parameters of aromatic carbonyl compounds may provide evidence as to the relationship between the electronic distribution of triplet states and the chemical reactivity of these states.

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