#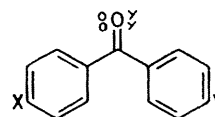 Merostabilization in Radical Ions, Triplets, and Biradicals.   Substituent Effects on the n,π* Triplet Energy of Benzophenone

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Summary An empirical approach is developed for the assessment of the importance of merostabilization in influencing the n,π* triplet energies of unsymmetrically substituted benzophenones.


(1)

X = Y = H: μ = 2·98 D

(2)   (3)

μ = 1·79 D

The stabilization imparted to free radicals bearing substituents of opposite electron demand, merostabilization,[1] is now an accepted phenomenon.   As part of our assessment of the importance of merostabilization in radical-like species,[2] we consider here the n,π* triplet state of substituted benzophenones (1a–i).

The substituent effect on the n,π* triplet energy of benzophenone[3] can be rationalized in terms of variation in charge redistribution between the ground and excited states. The measured dipole moments of these states indicate that the electron density on oxygen decreases upon excitation.[4] The triplet is described as the hybrid of valence bond structures (2) and (3).[5]   The electron density in (2) resembles that in the ground state and its energy should therefore be insensitive to substitution.   The energy of (3) will be subject to a more pronounced substituent effect since carbon bears a full negative charge.   Since the known substituent effects on
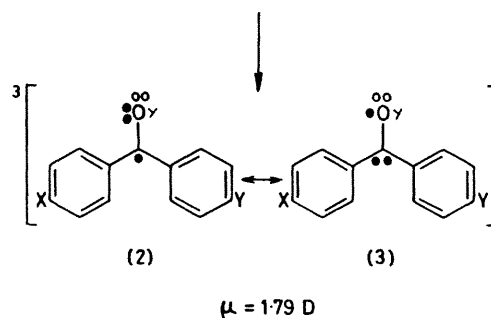
both electron delocalization in benzyl radicals[6] and the relative rates of decomposition of azocumenes[7] are small, it is reasonable to assume that the contributions to triplet energy

TABLE E_T^{n,π^*} and $E_{mero}^{X,Y}$ values for the benzophenones (1a—i).

	X	Y	E_T^{n,π^*}/(kJ mol⁻¹)[a]	$-E_{mero}^{X,Y}$/(kJ mol⁻¹)
a	H	H	289·5	
b	Me	Me	290·4	
c	OMe	OMe	292·0	
d	CN	CN	275·7	
e	Me	H	290·4	−0·4
f	OMe	H	290·4	0·4
g	H	CN	280·3	2·5
h	Me	CN	279·5	3·8
i	OMe	CN	278·7	5·4

[a] Ether–isopentane–alcohol (5:5:2) (EPA); 77 K. Values are reproducible to within ±0·8 kJ mol⁻¹.

from free-radical factors can usually be ignored.† The result then, is a correlation of n,π* triplet energy with Hammett σ_p-values (ρ is negative[3]). The small variation in triplet energy with substituent is consistent with the rather small difference in dipole moment between ground and excited states, which suggests that (2) is the dominant contributor to the hybrid structure. When X and Y are substituents of opposite electron demand, merostabilization of the radical-like triplet is possible; lowering of the triplet energy below that predicted on the basis of Hammett substituent constants should cause deviation from normal Hammett behaviour.
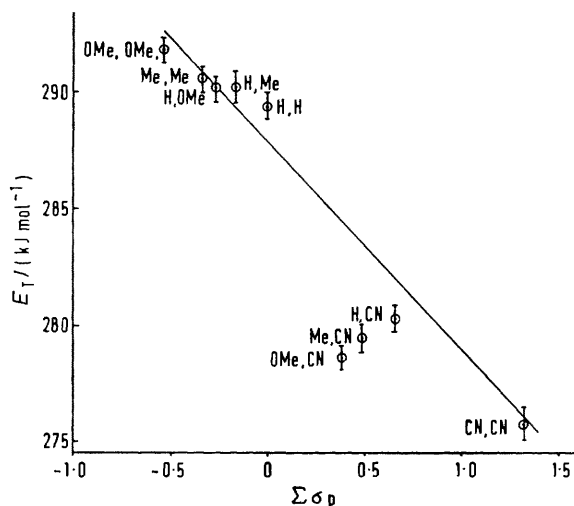

FIGURE 1 Hammett correlation for n,π* triplet energies (0–0 band) of benzophenones (1a—i) (EPA; 77 K).

The triplet energies (Table) are plotted against Hammett substituent constants $\Sigma\sigma_p$ in Figure 1. The least squares line is drawn for the symmetric derivatives (1a—d). While a good correlation exists for these derivatives (correlation coefficient 0·981), the points for the unsymmetrically substituted derivatives deviate from the line. For the cyano-substituted derivatives (1g—i), the deviation from normal Hammett behaviour increases with increasing electron-donating power of the X-group.

In the absence of merostabilization, substitution by a group X should cause half the effect of substitution by two symmetrically positioned X-groups. The estimated triplet energy for a monosubstituted system ($E_{est}^{X,Y}$) would then be the average of the observed triplet energies (E_{obs}) of the symmetrically disubstituted and unsubstituted derivatives. In general then, the triplet energy estimated for any unsymmetrically substituted system ($E_{est}^{X,Y}$) will be given by equation (1). We define *merostabilization energy* ($E_{mero}^{X,Y}$) as

$$E_{est}^{X,Y} = (E_{obs}^{X,X} + E_{obs}^{Y,Y})/2 \tag{1}$$

the difference between estimated and observed values of the energy [equation (2)]. We expect merostabilization energy

$$E_{mero}^{X,Y} = E_{obs}^{X,Y} - E_{est}^{X,Y} \tag{2}$$

to correlate with some combination of substituent constants indicating the difference in electron demand between the two substituents. A convenient parameter is $\Delta\sigma_{X,Y}$ [equation (3)], where X and Y are electron-donating and -accepting groups, respectively.
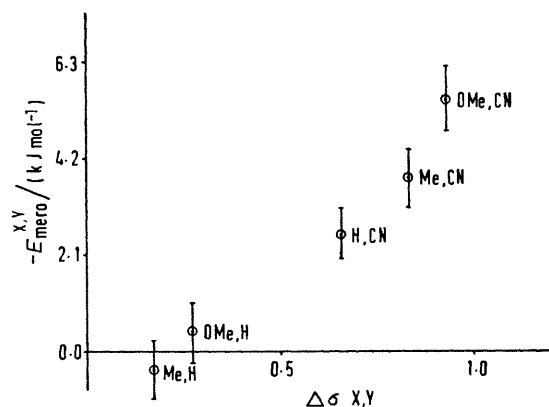
$$\Delta\sigma_{X,Y} = \sigma_Y - \sigma_X \tag{3}$$

FIGURE 2 Correlation of merostabilization energy with $\Delta\sigma_{X,Y}$.

An acceptable correlation between $E_{mero}^{X,Y}$ (Table) and $\Delta\sigma_{X,Y}$ is observed (Figure 2). This empirical approach

† *Added in Proof.* Results obtained after the submission of this manuscript indicate that E_T correlates better with a two-parameter equation incorporating Hammett σ-values and a set of parameters describing substituent effects on benzyl radical stability, and $E_{mero}^{X,Y}$ correlates better with $\Delta\sigma_{X,Y}^{\pm}$ (W. J. Leigh, D. R. Arnold, R. W. R. Humphreys, and P. C. Wong, *Can. J. Chem.*, in the press).

allows prediction of the extent to which merostabilization contributes to the energy of a system

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