EPR Spectra of 3,5-Disubstituted Benzyl Radicals

Richard A. Jackson* and Reza Moosavi
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, UK

A careful determination has been made of the EPR coupling constants of a series of seven 3,5-disubstituted benzyl radicals to assess the influence of *meta* substituents on delocalization of the unpaired electron. $a(CH_2)$ depends on σ_m (major component) and $\sigma_H^{\bullet}$ (minor component).

Benzylic radicals have played a prominent role in studies of substituent effects on free radical structure and reactivity. Substituent effects on the stability and reactivity of benzyl radicals would be expected to be more pronounced at *ortho* and *para* positions, where direct conjugation is possible, but effects have also been noticed from *meta* substituents on production of benzyl radicals from dibenzylmercury[1] (attributed to polar effects in the parent mercurial) and on the EPR spectra of benzyl radicals,[2–4] where, for example, the *meta*-fluorobenzyl radical has an α-CH_2 spin density higher than for benzyl itself.

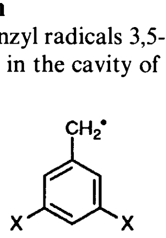
Dust and Arnold[3] suggested a linear relationship between stabilization and the α-CH_2 coupling constant of benzyl radicals (though the necessity for a linear relationship had previously been questioned).[1] They advanced the $\sigma_\alpha^{\bullet}$ scale as a measure of radical stabilization, and produced values for a number of *meta* and *para* substituents. A plot of $a(CH_2)$ for *meta*-substituted benzyl radicals *vs.* σ_m displayed an approximately linear dependence ($r^2 = 0.859$), indicating that electron-withdrawing substituents are associated with higher values of the α-CH_2 coupling constant.[4]

The range of effects of *meta* substituents is rather small [$a(CH_2)$ varies only over the range of *ca.* 0.5 G] and there is a significant difficulty in analysis of the EPR spectra, because the lack of symmetry gives doublet splittings for the four ring positions, compared with the triplet of triplets given by *para*-substituted compounds.

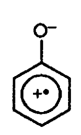
In an endeavour to increase the effects of the substituent and to obtain more easily and accurately analysable spectra, we turned to 3,5-disubstituted benzyl radicals, and report here our results on seven radicals of the type 3,5-$X_2C_6H_3CH_2^{\bullet}$.

Results and Discussion

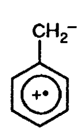
The 3,5-disubstituted benzyl radicals 3,5-$X_2C_6H_3CH_2^{\bullet}$ (**1**) were generated photolytically in the cavity of the EPR spectrometer from the corresponding toluene or benzyl bromide. A constant temperature of −40 °C was used, though it has been noted for unsubstituted benzyl radicals[5] that $a(CH_2)$ falls by only 0.12 G as the temperature is varied from ambient to 560 °C. Eight separate spectra were recorded for the unsubstituted benzyl radical (**1**, X = H), three for **1** (X = OCH_3 and Bu^t), and two for the other radicals. The results are collected in Table 1.



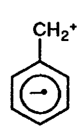
1



2



3



4

To analyse the spectra, we used the correlation programs[6] MATCH and SEEK, together with autocorrelation and the known values of α-, *ortho*- and *para*-couplings for the benzyl radical to provide starting values of coupling constants for the optimization.

Coupling constants were refined in three ways. In the first, MATCH was used to vary all the coupling constants and the spectrum linewidth systematically, one at a time, until the best fit with the experimental spectrum (using the product function—equivalent to the cross-correlation coefficient—as the criterion) was obtained. Although MATCH works with integer channel number values for coupling constants, values of coupling constants were estimated to an accuracy of 0.1 channel number by evaluating product-functions for each coupling separately at its 'best' value and at one channel unit up and down from this, and obtaining the maximum position from a quadratic fit. The coupling constants were calibrated on each occasion by running an Mn^{2+} spectrum (present as an impurity in SrO) at room temperature and taking the separation of the two central lines[7] (by autocorrelation) as 84.0 G.

In the second method, we refined the couplings using a routine FTMATCH which uses the fast Fourier transform (FFT) method to obtain simulated spectra to compare with the experimental one. The FFT method is not restricted to integer values of coupling constant, allowing the direct determination of coupling constants with a greater precision than is possible with integer methods. Goodness of fit was determined by cross-correlation with the experimental spectrum, and coupling constants were optimized using the quasi-Newton algorithm.[8] The coupling constants were calibrated against the manganese standard in the same way as was carried out for the first method.

In the third method, coupling constants for the α-positions were evaluated as in the first method, but calibration was carried out against a benzyl radical spectrum, obtained in the same series of experiments as that of the substituted benzyl radical, and at the same temperature. Use of this method avoids the need to return the EPR spectrometer to room temperature, necessary to maintain the distance between the two central manganese lines at 84.0 G.

The results display the consistency of the analytical methods. Using MATCH, the overall standard deviation from the determined means of all the coupling constants was 0.015 G. Our digitiser collected *ca.* 4000 points over a 100 G scan or 40 points per gauss, so this standard deviation indicates a precision of just over half a channel unit in the coupling constants. Since the recorder step-motor has only 1024 steps, the coupling constants have been determined to an accuracy of *ca.* $\frac{1}{7}$ of the

Table 1 EPR coupling constants for 3,5-$X_2C_6H_3CH_2^{\bullet}$ (**1**) (all coupling constants and standard deviations, sd, in Gauss)

X	No. of experiments	Position	MATCH		FTMATCH		Benzyl comparison	
			a	sd	*a*	sd	*a*	sd
H	8	α	16.352	0.013	16.356	0.009		
		o	5.177	0.005	5.181	0.003		
		m	1.771	0.008	1.773	0.008		
		p	6.203	0.010	6.192	0.011		
CF_3	2	α	16.635	0.018	16.634	0.016	16.646	0.010
		o	5.223	0.006	5.251	0.016		
		m	1.754	0.008	1.743	0.025		
		p	6.311	0.004	6.293	0.006		
OCH_3	3	α	16.285	0.021	16.285	0.022	16.259[c]	0.013
		o	5.032	0.015	5.032	0.008		
		m[a]	0.135	0.001	0.117	0.001		
		p	6.153	0.021	6.154	0.014		
F	2	α[b]	16.524	0.000	16.523	0.001		
		p[b]	5.086	0.005	5.092	0.004		
		m[b]	4.890	0.007	4.889	0.004		
		p[b]	6.121	0.025	6.135	0.018		
Bu^t	3	α	16.239	0.027	16.239	0.026	16.232	0.027
		o	5.084	0.033	5.087	0.024		
		m[a]	0.096	0.016	0.088	0.002		
		p	6.162	0.029	6.168	0.016		
Cl	2	α	16.504	0.025	16.521	0.029	16.491	0.017
		o	5.268	0.003	5.229	0.005		
		m[a]	0.228	0.006	0.376	0.001		
		p	6.305	0.016	6.297	0.007		
CH_3	2	α	16.203	0.004	16.205	0.004	16.191	0.004
		o	5.124	0.001	5.127	0.008		
		m	1.709	0.013	1.715	0.019		
		p	6.213	0.001	6.191	0.001		
Overall sd				0.015		0.013		0.018

[a] Buried in line width. Not used in comparison. [b] Not carried out on separate occasions. Not used in comparison. [c] Two values.

field-step: this result is attainable because the analytical method is using all the information in the spectrum (4000 points) to produce, for the benzyl radical, four coupling constants, the spectrum centre and the linewidth.

Use of FTMATCH produces a slightly lower overall standard deviation of 0.013. An F-test shows this is not significant at the 5% level. The result was disappointing: we expected that this non-integer method which uses significantly greater computer time would produce a substantial improvement in precision. However, since even with MATCH, coupling constants are being determined with a precision of *ca.* $\frac{1}{7}$ of the field-step, it may be that to expect significant improvement in precision is unrealistic.

The third analytical method, the comparison of couplings with the α-CH_2 coupling of a benzyl radical from a spectrum run in the same batch appears to give slightly less consistent results than the other methods, with an overall standard deviation of 0.018. However, this method does not require a field width of 100 G, with a resultant 'waste' of almost half the spectrum points so that if this method had been employed on its own, a scan width of *ca.* 60 G could have been selected.

During seven experimental sessions, the extremes of the measured distance between the two central manganese lines varied by only 11 channel numbers or *ca.* 0.35%. Not allowing for this would have produced an error of *ca.* ±0.03 G in the α-coupling constants at the extremes and shows that the calibration of each batch was worthwhile.

α-CH_2 *Coupling Constants in* meta *and* 3,5-*Disubstituted Benzyl Radicals*.—There appears from the literature [2–4] to be a trend for electron-withdrawing substituents at the *meta* position to increase spin density at the α-CH_2 position of benzyl free radicals, and a plot of $a(CH_2)$ *vs.* σ_m gave an approximately straight line. However, 3,5-disubstituted benzyl radicals have spectra from which couplings can be determined more unequivocally,* and the effects of the substituents should be larger. This proves to be the case, but a plot of the α-CH_2 coupling constants for the 3,5-disubstituted benzyl radicals *vs.* those of the *meta*-substituted radicals shows a slope of 1.34 ± 0.23 ($r^2 = 0.893$), considerably less than the value of 2.0 expected if substituent effects are additive.

The results from our series of seven 3,5-disubstituted benzyl radicals show that there is a general association of electron-releasing substituents with high $a(CH_2)$, but a straight-line plot (Fig. 1) shows considerable scatter ($r^2 = 0.921$). The standard

---

* As expected, the couplings obtained for ring positions in 3,5-disubstituted benzyl radicals are similar to those for equivalent positions in the corresponding *meta*-substituted radicals. However, our value of 1.71 G for the 3,5-dimethyl CH_3 protons is substantially less than that reported by Dust and Arnold [3] for the CH_3 protons in *m*-xylyl (3.38 G), but is in better agreement with an earlier value [9] of 1.66 G for this coupling constant. On the basis that methyl substituents on aromatic rings have CH_3 coupling constants approximately equal to those of the hydrogens they replace, the lower values appear more likely.

Table 2 UMINDO calculations on $3,5\text{-}X_2C_6H_3CH_2^{\bullet}$ and $3,5\text{-}X_2C_6H_3CH_3$

X	Benzylic H spin density[a]	ΔH_f/kJ mol^{-1}		ΔH_1/kJ mol^{-1}
		$3,5\text{-}X_2C_6H_3CH_2^{\bullet}$	$3,5\text{-}X_2C_6H_3CH_3$	
OCH_3	−0.0122	−179.7	−306.9	+4.4
F	−0.0121	−202.5	−328.3	+3.0
CF_3	−0.0115	−1231.4	−1355.1	+0.9
H	−0.0124	216.0	93.2	0.0
Cl	−0.0117	147.1	24.8	−0.4
CH_3	−0.0112	164.0	43.2	−2.0
Bu^t	−0.0111	275.5	155.1	−2.3

[a] Annihilated.

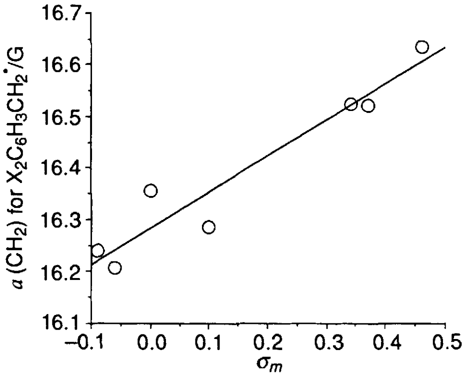


Fig. 1 Plot of $a(CH_2)$ for $3,5\text{-}X_2C_6H_3CH_2^{\bullet}$ *vs.* σ_m

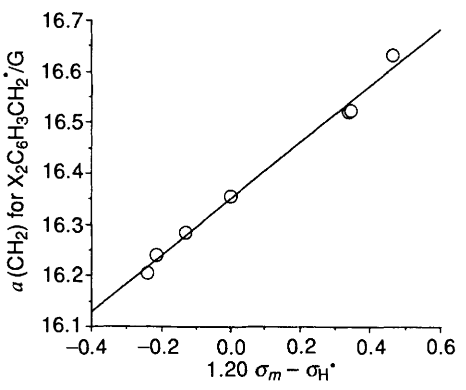


Fig. 2 Plot of $a(CH_2)$ for $3,5\text{-}X_2C_6H_3CH_2^{\bullet}$ *vs.* $1.20\ \sigma_m - \sigma^{\bullet}_H$

deviation of the experimental $a(CH_2)$ values from the regression line was 0.05, considerably greater than the experimental error (0.013), indicating that further factor(s) are important. Plots of $a(CH_2)$ *vs.* σ_p^-, σ_p, σ_p^+ and $\sigma^{\bullet}_H$ give worse correlations (r^2 = 0.888, 0.811, 0.624 and 0.178 respectively).

A multiple regression approach showed that the best fit for two dependent variables was obtained using σ_m and $\sigma^{\bullet}_H$ ($r^2 = 0.990$). The parameter σ_m is a measure of mainly inductive polar electron release or withdrawal;[10] $\sigma^{\bullet}_H$ was chosen as a measure of radical stabilization[11] because unlike other measures of radical stabilization, it is defined in terms of σ, σ_p^+ and σ_p^- and therefore values are available for a much wider range of substituents, compared with other scales.[1,12] The best fit was found for $a(CH_2) = (0.668 \pm 0.036)\sigma_m - (0.557 \pm 0.103)\sigma^{\bullet}_H + 16.351$, and in Fig. 2, a plot of $a(CH_2)$ *vs.* $1.20\sigma_m - \sigma^{\bullet}_H$, shows that all points are within two standard deviations [experimental precision of the $a(CH_2)$ values] from the line.

The interpretation of these substituent effects is difficult. To a first (Hückel) approximation, there should be no effect of substituents on the unstarred 3 and 5 positions of the benzyl radical. Calculations at various levels of sophistication are unimpressive in predicting for example the approximate α/p ratio for coupling constants. In the hope that even if predictions of absolute coupling constants were unreliable, changes caused by substituents might be more tractable, we calculated α-CH_2 spin densities by the semiempirical UMINDO method for all our compounds (Table 2), but no significant correlation with our experimental values was seen. We also calculated ΔH for the isodesmic reaction (1), but no significant correlation was

$$ArCH_3 + C_6H_5CH_2^{\bullet} \longrightarrow ArCH_2^{\bullet} + C_6H_5CH_3 \quad (1)$$

found between ΔH for this reaction and $a(CH_2)$. However, in view of the small spread in ΔH values and the large probable errors in the computed values, not all of which will cancel out, this cannot be considered to be reliable evidence against a connection between $a(CH_2)$ and stabilization energy.

A helpful clue may come from consideration of phenoxyl radicals. Electron-releasing substituents at the *para* position weaken the ArO–H bond, presumably by stabilizing the $ArO^{\bullet}$ radical.[13] A σ^+ dependence is found, suggesting that in resonance terms, **2** may contribute significantly to the structure of the phenoxyl radical. If the analogous structure **3** similarly contributes to the structure of the benzyl radical, the dependence of $a(CH_2)$ on both σ_m and $\sigma^{\bullet}_H$ is explained. Electron-releasing (negative σ_m) and radical-stabilizing (high $\sigma^{\bullet}_H$) substituents will stabilize **3**, increase its contribution, and therefore reduce the spin density at the α-position; conversely, electron-withdrawing groups (on this picture there are no radical destabilizing groups) will increase the spin density at the α-position.

In the case of the phenoxyl radical, the electronegativity of the oxygen atom ensures that if there are polar contributions, they will be of type **2** rather than having positive charge on the oxygen and negative charge on the ring. In accord with this, bond dissociation energies E_{bd}(ArO–H) have been found to correlate with σ^+ values of substituents at the *para* position.[13]

For benzyl, the polarity is not so obvious. It may be that since antibonding orbitals are in general more antibonding than the corresponding bonding orbital is bonding, structure **3** with an electron removed from the highest occupied molecular orbital (HOMO) of benzene will have a lower energy than **4** which has an electron added to the LUMO. In support of this, we find that both *ab initio* (GAUSSIAN82 STO–3G) and semiempirical (UMINDO) calculations show a negative charge on the α-carbon atom.

para-*Substituted Benzyl Radicals.*—In the light of the above discussion, it might be expected that *para*-substituted benzyl radicals will also show a dependence on σ and $\sigma^{\bullet}_H$, with a greater influence of $\sigma^{\bullet}_H$ compared with the *meta* position. Three sets of data exist,[1,3,14] with 7, 12 and 7 uncharged substituents, respectively. The first two sets are in organic solvents, the third in water. Multiple-regression analysis of the data of Dinçtürk, Jackson *et al.*[1] shows that the best one-component fit is with $\sigma^{\bullet}_{\mathrm{H}}$ with $r^2 = 0.906$. The best two-component fit is with $\sigma^{\bullet}_{\mathrm{H}}$ and $\sigma^{\bullet}_{p}$; r^2 increases to 0.995, and the regression eqn. (2) fits the points with a standard deviation

$$a(\mathrm{CH_2}) = (-2.439 \pm 0.124)\sigma^{\bullet}_{\mathrm{H}} - (0.406 \pm 0.049)\sigma_p + 16.45 \quad (2)$$

of 0.04 G. Dust and Arnold's[3] and Neta and Schuler's[14] data both correlate best with $\sigma^{\bullet}_{\mathrm{H}}$ with slopes of -2.87 and -3.04, and $r^2 = 0.866$ and 0.873, respectively, but without significant improvement on inclusion of a second component. An overall set of data, obtained by combining $a(\mathrm{XC_6H_4CH_2^{\bullet}}) - a(\mathrm{C_6H_5CH_2^{\bullet}})$ data from the three sets to minimize differences caused by the small differences in $a(\mathrm{C_6H_5CH_2^{\bullet}})$ reported by the three groups gave a set of eight values common to two or more of the sets. Here again, the best simple correlation was with $\sigma^{\bullet}_{\mathrm{H}}$ ($r^2 = 0.920$), improved to $r^2 = 0.969$ by taking account of $\sigma^{\bullet}_{\mathrm{H}}$ and σ_p, with a standard deviation for predicted values of 0.09 G [eqn. (3)].

$$a(\mathrm{X}) - a(\mathrm{H}) = (-2.49 \pm 0.28)\sigma^{\bullet}_{\mathrm{H}} - (0.33 \pm 0.12)\sigma_p + 0.089 \quad (3)$$

However, combination of the three sets of data showed that the standard deviation of the values from the means was 0.14 G (compared with the value of 0.013 G for the *meta* values determined in this work). It therefore appears desirable that a more careful determination of the coupling constants of *para*-substituted benzyl radicals should be made, with replicate determinations for each substituent, in view of the importance of this data in discussions of radical stabilization and reactivity, and the interplay between radical and polar effects.

Experimental

3,5-Dichlorobenzyl chloride was prepared by treating the alcohol with thionyl chloride.[15] The other precursors were available commercially, and were >98% pure by GC.

EPR experiments were carried out at -40 °C in the cavity of a Varian E104A spectrometer, under UV irradiation from a 1 kW Hg/Xe Hanovia lamp. Samples consisted of *tert*-butyl peroxide and 3,5-$\mathrm{X_2C_6H_3CH_3}$ (X = H, $\mathrm{OCH_3}$, $\mathrm{CH_3}$, $\mathrm{Bu^t}$) (*ca.* 3:1 v/v) or *tert*-butyl peroxide, triethylsilane and 3,5-$\mathrm{X_2C_6H_3CH_2Br}$ (X = $\mathrm{CF_3}$, F, H) or 3,5-$\mathrm{X_2C_6H_3CH_2Cl}$ (X = Cl) (*ca.* 5:2:1 v/v). Calibration was carried out before or after each batch of experiments using the central two lines[7] of $\mathrm{Mn^{2+}}$ (present as an impurity in strontium oxide). The separation of these two lines which are 84.0 G apart was determined by autocorrelation; the calibrations were carried out at room temperature.

UMINDO calculations[16] were carried out with optimized geometry, with the aromatic carbon atoms and all atoms adjacent to a ring carbon constrained to the plane of the ring.

References

1 S. Dinçtürk, R. A. Jackson, M. Townson, H. Ağirbaş, N. C. Billingham and G. March, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1121.
2 A. Hudson and J. W. E. Lewis, *Mol. Phys.*, 1970, **19**, 241.
3 J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, 1983, **105**, 1221, 6531.
4 D. D. M. Wayner and D. R. Arnold, *Can. J. Chem.*, 1985, **63**, 2378.
5 R. Livingston, H. Zeldes and M. S. Conradi, *J. Am. Chem. Soc.*, 1979, **101**, 4312.
6 R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1983, 523; R. A. Jackson and C. J. Rhodes, *J. Chem. Soc., Perkin Trans. 2*, 1985, 121.
7 J. Rosenthal and L. Yarmus, *Rev. Sci. Instrum.*, 1966, **37**, 381; H. M. Swarz, J. R. Bolton and D. C. Borg, *Biological Applications of Electron Spin Resonance*, Wiley, New York, 1972.
8 P. E. Gill and W. Murray, National Physical Laboratory report NAC72, 1976 (through Numerical Algorithms Group Fortran Library Manual, Mark 14, Oxford, 1990).
9 M. S. Conradi, H. Zeldes and R. Livingston, *J. Phys. Chem.*, 1979, **83**, 633.
10 Values for Hammett-type substituent constants were taken from: O. Exner, *Correlation Analysis of Chemical Data*, Plenum, New York, 1988.
11 S. Dinçtürk and R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1127; R. A. Jackson in *Substituent Effects in Radical Chemistry*, eds. H. G. Viehe, Z. Janousek and R. Merényi, D. Reidel, Dordrecht, 1986, p. 325.
12 T. Yamamoto and T. Otsu, *Chem. Ind.*, 1967, 787; H. Sakurai, S. Hayashi and A. Hosomi, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1945; R. Itô, T. Migita, N. Morikawa and O. Simamura, *Tetrahedron*, 1965, **21**, 955; T. H. Fisher and A. W. Meierhoefer, *J. Org. Chem.*, 1978, **43**, 224; X. Creary, *J. Org. Chem.*, 1980, **45**, 280; H. Ağirbaş and R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1983, 739.
13 P. Mulder, O. W. Saastad and D. Griller, *J. Am. Chem. Soc.*, 1988, **110**, 4090; J. Lind, X. Shen, T. E. Eriksen and G. Merényi, *J. Am. Chem. Soc.*, 1990, **112**, 479.
14 P. Neta and R. H. Schuler, *J. Phys. Chem.*, 1973, **77**, 1368.
15 M. S. Newman, *J. Am. Chem. Soc.*, 1940, **62**, 2295.
16 P. Bischof, *J. Am. Chem. Soc.*, 1976, **98**, 6844.

Paper 2/00340F
Received 21*st January* 1992
Accepted 25*th February* 1992