Improved method for estimating the ZFS parameter *D* for delocalized biradicals

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ABSTRACT: An 'average' approximation for calculating the zero-field splitting parameter, *D*, gives reasonable results when used to calculate *D* values for non-disjoint delocalized organic biradicals. When used to calculate disjoint localized organic biradicals the *D* values are approximately half the experimental values. © 1998 John Wiley & Sons, Ltd.

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Calculating zero-field splitting (ZFS) parameters, *D* and *E*, as a function of molecular geometry is one of the few methods available for elucidating the conformations of organic molecules having more than one unpaired electron.[1,2] The ZFS parameter *D* gives an indication of the dipolar interaction of unpaired electrons in molecules in the absence of spin–orbit coupling and therefore is related to interelectronic distance.

Rigorous theoretical determinations of *D* using high-quality *ab initio* wavefunctions have been performed for the excited-triplet states of formaldehyde,[3] benzene and naphthalene[4] and ground-triplets states of methylene[5] and trimethylenemethane.[6] Although it is theoretically possible to determine *D* with *ab initio* basis sets and electron correlation, it may not be computationally practical—a fact which has led to the derivation of approximate methods to simplify the task of evaluating the large number of integrals involved for even moderate-sized molecules.[7] These various approximations used for the theoretical determination of *D* have been presented in the literature over the last several decades.[1,4,8–21]

An approximation which is frequently used by Mukai and co-workers[1,19,20] is

$$D = \frac{3}{4} g^2 \beta^2 \sum_{i,j} \frac{r_{ij}^2 - 3m_{ij}^2}{r_{ij}^5} \rho_i \rho_j \qquad (1)$$
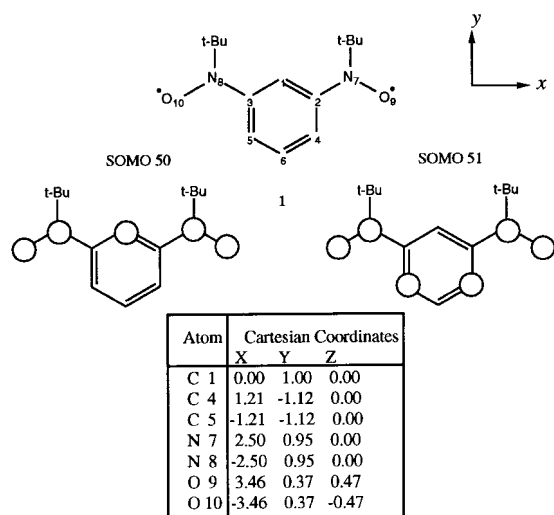
where r_{ij} is the distance between atoms i and j, m_{ij} is the distance vector along the axis which gives rise to the

largest dipole–dipole interaction and ρ_i and ρ_j are the spin densities on atoms i and j. This equation has been used to give reasonable *D* value approximations for biradicals with localized electron distributions that can be separated into monoradical halves with atoms i and j belonging to different halves (hereafter referred to as localized biradicals.) The spin densities used are those of each monoradical half. It has been noted that this equation provides only crude approximations for delocalized biradicals,[21] which initiated an investigation in our laboratory into finding a *simple* approximate method that would provide more reasonable *D* values for delocalized biradicals owing to our interest in moderate-sized non-disjoint organic molecules with $S > 1/2$.[22] The problem we encountered in trying to use Eqn (1) for delocalized radical systems was that the delocalized system could not be separated into monoradical halves due to shared spin-containing atoms (hereafter referred to as delocalized biradicals). Since the dipole–dipole interaction, and thus the *D* value, strongly depend on the average distance between the two unpaired electrons (varying as $1/r^3$),[23] the question is how one determines the 'average' distance. With this in mind, we found a phenomenological method with which we have been able to calculate reasonable *D* values for delocalized biradicals. The method entails the use of average r^2, r^5 and m^2 to determine the 'average' interelectronic distance:

$$D = \frac{3}{4} g^2 \beta^2 \left[\frac{\langle r_{ij}^2 \rangle - 3\langle m_{ij}^2 \rangle}{\langle r_{ij}^5 \rangle} \right] \qquad (2)$$

where atom i is a spin-containing atom (spin density ≥ 0.01) in one SOMO and atom j is a spin-containing atom (also with spin density ≥ 0.01) in the other SOMO, and r_{ij} refers to the distance between spin-containing

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1

Atom	Cartesian Coordinates		
	X	Y	Z
C 1	0.00	1.00	0.00
C 4	1.21	-1.12	0.00
C 5	-1.21	-1.12	0.00
N 7	2.50	0.95	0.00
N 8	-2.50	0.95	0.00
O 9	3.46	0.37	0.47
O 10	-3.46	0.37	-0.47

atoms in the SOMOs instead of the monoradical halves since the biradical cannot be separated into monoradical halves owing to its non-disjoint nature. The spin density is determined by summing the squared coefficients (obtained from AM1–RHF–triplet calculation[24]) of each atom in the SOMO. Since the sum of the product $\rho_i\rho_j$ is approximately unity, we found its inclusion in the calculation unnecessary. Based on the Pauli exclusion principle we assigned a value of zero for the term when $i = j$. Table 1 gives an example of the calculation method for dinitroxide **1**.

From Table 1, D_{av} is calculated as follows:

$$D = \frac{3}{4}g^2\beta^2\left[\frac{\langle r_{ij}^2\rangle - 3\langle m_{ij}^2\rangle}{\langle r_{ij}^5\rangle}\right]$$

$$= \frac{3}{4}g^2\beta^2\left(\frac{17.66 - 3 \times 15.99}{3131.29}\right) = -0.01260 \text{ cm}^{-1}$$
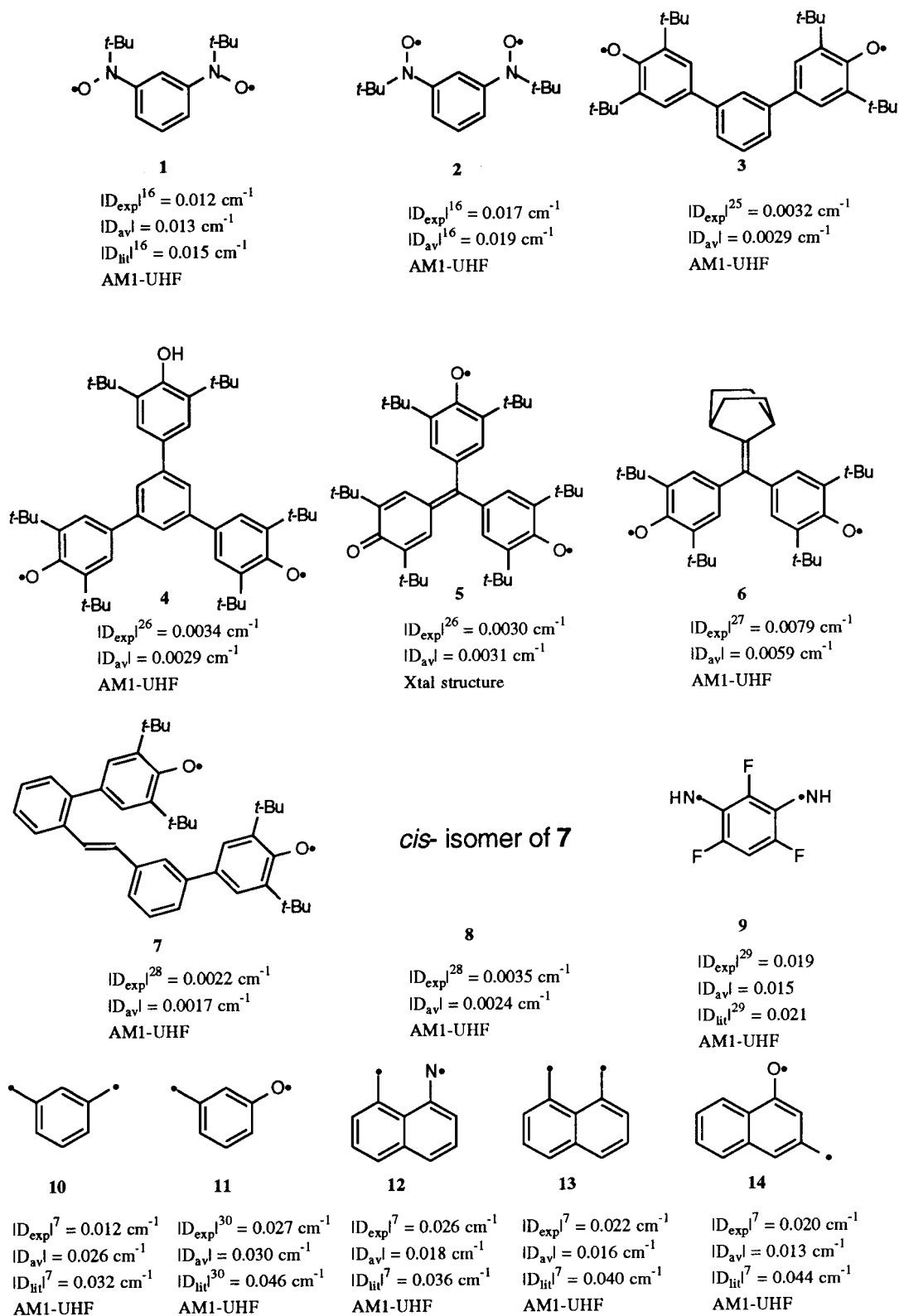
$$(|D_{exp}| = 0.0122 \text{ cm}^{-1})$$

In this example, the largest dipole–dipole interaction is along the x-axis, therefore $\langle m_{ij}^2\rangle$ is $\langle x_{ij}^2\rangle$. The aspect of this approximation needed to obtain reasonable D-values is the use of $\langle r^2\rangle$ and $\langle r^5\rangle$, not $\langle r\rangle^2$ and $\langle r\rangle^5$ as demonstrated in the following example.

$$D = \frac{3}{4}g^2\beta^2\left(\frac{14.36 - 3 \times 15.99}{784.17}\right) = -0.05579 \text{ cm}^{-1} \quad (3)$$

The equation is the calculation for **1** where $\langle r^2\rangle$ and $\langle r^5\rangle$ have been substituted by $\langle r\rangle^2$ and $\langle r\rangle^5$ ($\langle r\rangle = 3.79$).

The $|D|$ value obtained from Eqn (2) of 0.0126 cm^{-1} (Table 1) is much closer to the experimental result (0.012 cm^{-1}) than the $|D|$ value obtained from Eqn (3) of 0.056 cm^{-1}. The $|D|$ value obtained for **1** using Eqn (1), 0.22 cm^{-1}, where ij represents all the possible atom combinations (no separation of atoms into SOMOs or radical halves) and $\rho_i\rho_j$ is the product of spin densities on

Table 1. Example of D_{av} calculation[a]

Atom (SOMO)	$(x_i - x_j)$	$(y_i - y_j)$	$(z_i - z_j)$	x_{ij}^2	y_{ij}^2	z_{ij}^2	r_{ij}^2	r_{ij}^5
C1(50)—C4(51)	−1.21	2.12	0.00	1.47	4.51	0.00	5.98	87.59
C1(50)—C5(51)	1.21	2.12	0.00	1.47	4.51	0.00	5.98	87.59
C1(50)—N7(51)	−2.50	0.05	0.00	6.24	0.00	0.00	6.25	97.53
C1(50)—N8(51)	2.50	0.05	0.00	6.24	0.00	0.00	6.25	97.53
C1(50)—O9(51)	−3.46	0.63	−0.47	11.98	0.40	0.22	12.60	563.91
C1(50)—O10(51)	3.46	0.63	0.47	11.98	0.40	0.22	12.60	563.91
C4(51)—N7(50)	−1.28	−2.08	0.00	1.65	4.31	0.00	5.96	86.60
C4(51)—N8(50)	3.71	−2.08	0.00	13.79	4.31	0.00	18.09	1392.10
C4(51)—O9(50)	−2.25	−1.49	−0.47	5.05	2.22	0.22	7.49	153.79
C4(51)—O10(50)	4.68	−1.49	0.47	21.86	2.22	0.22	24.30	2911.45
C5(51)—N7(50)	−3.71	−2.08	0.00	13.79	4.31	0.00	18.09	1392.10
C5(51)—N8(50)	1.28	−2.08	0.00	1.65	4.31	0.00	5.96	86.60
C5(51)—O9(50)	−4.68	−1.49	−0.47	21.86	2.22	0.22	24.30	2911.45
C5(51)—O10(50)	2.25	−1.49	0.47	5.05	2.22	0.22	7.49	153.79
N7(50)—N8(51)	5.00	0.00	0.00	24.98	0.00	0.00	24.98	3118.13
N7(50)—O9(51)	−0.96	0.58	−0.47	0.93	0.34	0.22	1.49	2.71
N7(50)—O10(51)	5.96	0.58	0.47	35.52	0.34	0.22	36.09	7822.72
N7(51)—N8(50)	5.00	0.00	0.00	24.98	0.00	0.00	24.98	3118.13
N7(51)—O9(50)	−0.96	0.58	−0.47	0.93	0.34	0.22	1.49	2.71
N7(51)—O10(50)	5.96	0.58	0.47	35.52	0.34	0.22	36.09	7822.72
N8(50)—O9(51)	−5.96	0.58	−0.47	35.52	0.34	0.22	36.09	7822.72
N8(50)—O10(51)	0.96	0.58	0.47	0.93	0.34	0.22	1.49	2.71
N8(51)—O9(50)	−5.96	0.58	−0.47	35.52	0.34	0.22	36.09	7822.72
N8(51)—O10(50)	0.96	0.58	0.47	0.93	0.34	0.22	1.49	2.71
O9(50)—O10(51)	6.92	0.00	0.95	47.92	0.00	0.89	48.81	16644.77
O9(51)—O10(50)	6.92	0.00	0.95	47.92	0.00	0.89	48.81	16644.77
Average				15.99	1.49	0.19	17.66	3131.29

[a] Lengths in Å.

1

$|D_{exp}|^{16} = 0.012 \text{ cm}^{-1}$
$|D_{av}| = 0.013 \text{ cm}^{-1}$
$|D_{lit}|^{16} = 0.015 \text{ cm}^{-1}$
AM1-UHF

2

$|D_{exp}|^{16} = 0.017 \text{ cm}^{-1}$
$|D_{av}|^{16} = 0.019 \text{ cm}^{-1}$
AM1-UHF

3

$|D_{exp}|^{25} = 0.0032 \text{ cm}^{-1}$
$|D_{av}| = 0.0029 \text{ cm}^{-1}$
AM1-UHF

4

$|D_{exp}|^{26} = 0.0034 \text{ cm}^{-1}$
$|D_{av}| = 0.0029 \text{ cm}^{-1}$
AM1-UHF

5

$|D_{exp}|^{26} = 0.0030 \text{ cm}^{-1}$
$|D_{av}| = 0.0031 \text{ cm}^{-1}$
Xtal structure

6

$|D_{exp}|^{27} = 0.0079 \text{ cm}^{-1}$
$|D_{av}| = 0.0059 \text{ cm}^{-1}$
AM1-UHF

7

$|D_{exp}|^{28} = 0.0022 \text{ cm}^{-1}$
$|D_{av}| = 0.0017 \text{ cm}^{-1}$
AM1-UHF

cis- isomer of **7**

8

$|D_{exp}|^{28} = 0.0035 \text{ cm}^{-1}$
$|D_{av}| = 0.0024 \text{ cm}^{-1}$
AM1-UHF

9

$|D_{exp}|^{29} = 0.019$
$|D_{av}| = 0.015$
$|D_{lit}|^{29} = 0.021$
AM1-UHF

10

$|D_{exp}|^{7} = 0.012 \text{ cm}^{-1}$
$|D_{av}| = 0.026 \text{ cm}^{-1}$
$|D_{lit}|^{7} = 0.032 \text{ cm}^{-1}$
AM1-UHF

11

$|D_{exp}|^{30} = 0.027 \text{ cm}^{-1}$
$|D_{av}| = 0.030 \text{ cm}^{-1}$
$|D_{lit}|^{30} = 0.046 \text{ cm}^{-1}$
AM1-UHF

12

$|D_{exp}|^{7} = 0.026 \text{ cm}^{-1}$
$|D_{av}| = 0.018 \text{ cm}^{-1}$
$|D_{lit}|^{7} = 0.036 \text{ cm}^{-1}$
AM1-UHF

13

$|D_{exp}|^{7} = 0.022 \text{ cm}^{-1}$
$|D_{av}| = 0.016 \text{ cm}^{-1}$
$|D_{lit}|^{7} = 0.040 \text{ cm}^{-1}$
AM1-UHF

14

$|D_{exp}|^{7} = 0.020 \text{ cm}^{-1}$
$|D_{av}| = 0.013 \text{ cm}^{-1}$
$|D_{lit}|^{7} = 0.044 \text{ cm}^{-1}$
AM1-UHF

Scheme 1

atoms i and j obtained from an AM1 RHF-CI TRIP calculation (including negative spin densities). Using Eqn (1) where i represents atoms in SOMO i and j represents atoms in SOMO j and ρ_i is the spin density obtained from the sum of the coefficients squared on atom i in SOMO i (and likewise for j), we obtained a $|D|$ value of 0.0974 cm^{-1}. Comparison of the results from these calculations demonstrates that Eqn (2) is the only

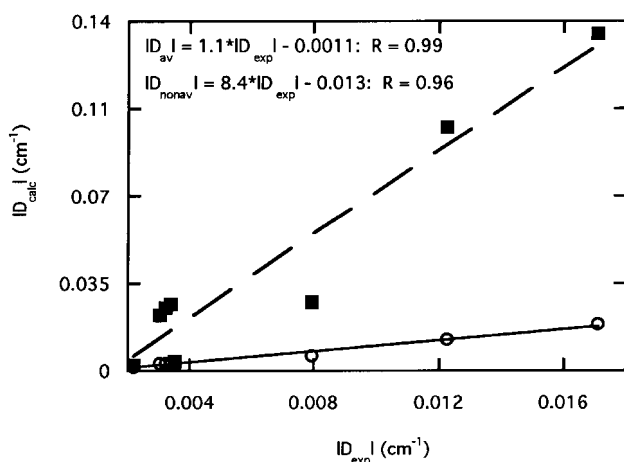**Figure 1.** ZFS parameter D: $|D_{calc}|$ vs $|D_{exp}|$ for delocalized non-disjoint phenoxy and nitroxy biradicals. (■) D values obtained from Eqn (10) (D_{nonav}); (○) D values obtained from Eqn (11) (D_{av})

Figure 2. ZFS parameter D: $|D_{calc}|$ vs $|D_{exp}|$ for delocalized non-disjoint biradicals. (■) Calculated D values cited in the literature ($D_{lit.calc.}$); (○) D values obtained from Eqn (11) (D_{av})

approximate method examined that gives a reasonable $|D|$ value. We are not claiming a theoretically rigorous connection between Eqns (1) and (2). What we have found is a seemingly successful phenomenological approach for calculating the D value for non-disjoint nitroxy and phenoxy radicals.

The interest in stable biradicals and thus the focus on nitroxy and phenoxy radicals is amply reflected in the literature. Our calculation results, comprised of only delocalized bisphenoxy and bisnitroxy biradicals **1–8** in Scheme 1 are very promising. Figure 1 is a plot of the calculated D values using Eqn (1) (D_{nonav}) (where, again, i and j refer to the non-disjoint SOMOs), and Eqn (2) (D_{av}) versus the experimental D values for biradicals **1–8**. We included less stable carbon-based biradicals and other biradicals that are not bisphenoxy- or bisnitroxy-based (hereafter referred to as non-bisoxy biradicals) (**9–14**) in this investigation to see how applicable the approximation method was for other delocalized non-disjoint biradicals. Figure 2 is a plot of all of the compounds given in Scheme 1. The non-bisoxy biradicals **9–14** deviate from the linearity of the bisoxy biradicals **1–8** as seen in Fig. 2, but are closer to the experimental results than the calculated results obtained by various other approximations reported in the literature. We limited the compounds reported to those non-disjoint biradicals which have the fewest torsions due to the geometrical sensitivity of the calculation.

The geometries of compounds **1–4** and **6–14** were obtained from optimized AM1–triplet UHF calculations.[24] Coordinates from the x-ray crystal structure were used for compound **5**.[31]

For localized disjoint biradicals, Eqn (2) gives a D value that is approximately half the experimental value, as seen in Fig. 3 for the localized biradicals given in Scheme 2. The need for an empirical factor to make the
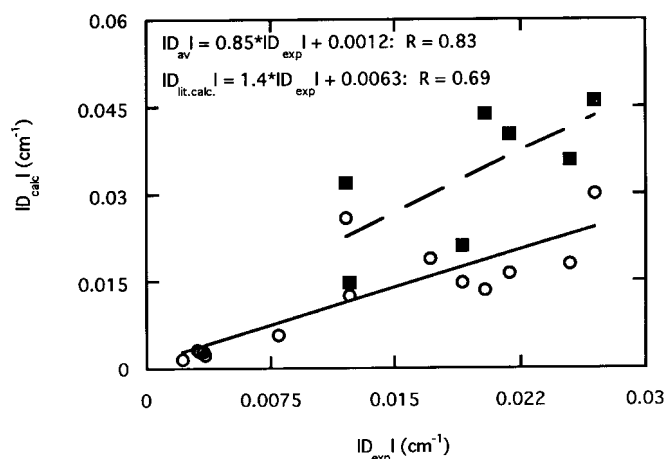
calculated values agree with experimental values is not unique to our approximate method.[7,32]

The geometries of compounds **15–23** were obtained from optimized AM1–triplet UHF calculations.[24] Coordinates from the x-ray crystal structure were used for compound **24**.[34]

An important point is that many of the calculated literature values were obtained from calculations which were performed at various twist angles between rings. The dihedral angle which resulted in the D value closest to the experimental value is cited as the calculated value.[1,2,17,19,20] Our calculations, on the other hand, are based on just one geometry—the optimized dihedral. Obtaining a correlation coefficient of 0.99 for the localized biradicals with just one shot at the target is impressive.

Equation (2) can be used not only for non-disjoint biradicals to predict the D values, but also to predict the
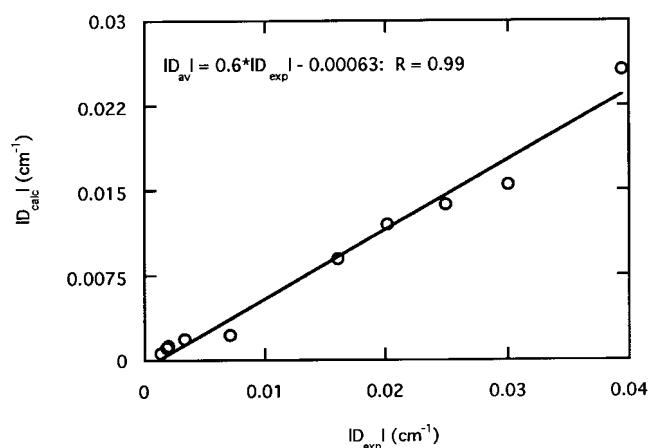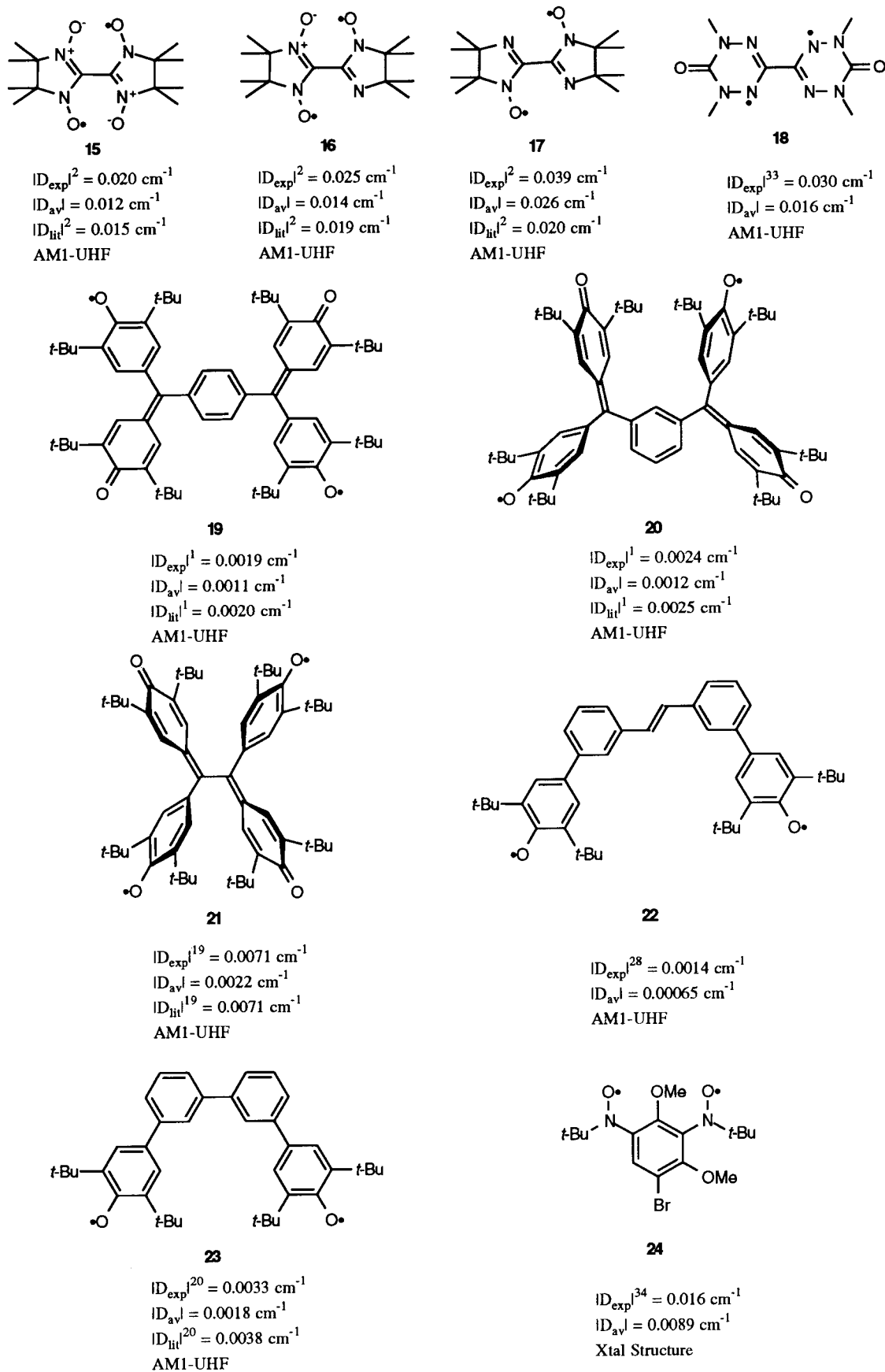

Figure 3. ZFS parameter D: $|D_{calc}|$ vs $|D_{exp}|$ for localized biradicals. (○) D values obtained from Eqn (11) (D_{av})

15

$|D_{exp}|^2 = 0.020$ cm^{-1}
$|D_{av}| = 0.012$ cm^{-1}
$|D_{lit}|^2 = 0.015$ cm^{-1}
AM1-UHF

16

$|D_{exp}|^2 = 0.025$ cm^{-1}
$|D_{av}| = 0.014$ cm^{-1}
$|D_{lit}|^2 = 0.019$ cm^{-1}
AM1-UHF

17

$|D_{exp}|^2 = 0.039$ cm^{-1}
$|D_{av}| = 0.026$ cm^{-1}
$|D_{lit}|^2 = 0.020$ cm^{-1}
AM1-UHF

18

$|D_{exp}|^{33} = 0.030$ cm^{-1}
$|D_{av}| = 0.016$ cm^{-1}
AM1-UHF

19

$|D_{exp}|^1 = 0.0019$ cm^{-1}
$|D_{av}| = 0.0011$ cm^{-1}
$|D_{lit}|^1 = 0.0020$ cm^{-1}
AM1-UHF

20

$|D_{exp}|^1 = 0.0024$ cm^{-1}
$|D_{av}| = 0.0012$ cm^{-1}
$|D_{lit}|^1 = 0.0025$ cm^{-1}
AM1-UHF

21

$|D_{exp}|^{19} = 0.0071$ cm^{-1}
$|D_{av}| = 0.0022$ cm^{-1}
$|D_{lit}|^{19} = 0.0071$ cm^{-1}
AM1-UHF

22

$|D_{exp}|^{28} = 0.0014$ cm^{-1}
$|D_{av}| = 0.00065$ cm^{-1}
AM1-UHF

23

$|D_{exp}|^{20} = 0.0033$ cm^{-1}
$|D_{av}| = 0.0018$ cm^{-1}
$|D_{lit}|^{20} = 0.0038$ cm^{-1}
AM1-UHF

24

$|D_{exp}|^{34} = 0.016$ cm^{-1}
$|D_{av}| = 0.0089$ cm^{-1}
Xtal Structure

Scheme 2

geometries of the biradicals. Experimental D values for conformations **1** and **2** show that D is dependent on geometry, and our calculation results reflect this dependence well.

The D_{av} values for two of the smallest non-disjoint delocalized biradicals, m-xylylene (MPH) and trimethylenemethane (TMM), are approximately two and four times the experimental values,[7,35] respectively (MPH, $D_{av} = 0.026\ cm^{-1}$, $D_{exp} = 0.012\ cm^{-1}$; TMM, $D_{av} = 0.09\ cm^{-1}$, $D_{exp} = 0.024\ cm^{-1}$). We cannot explain why the calculated D values for MPH, TMM and the localized biradicals deviate from the experimental values. It should be noted that this approximation is based strictly on distance and positive spin densities; spin–orbit coupling and negative spin densities have not been taken into account. The neglect of negative spin densities,[10] which are significant in both MPH and TMM, might account for the large deviation observed in the calculated D values. Although this method is strictly empirical and limited in its scope for predicting reasonable D values to non-disjoint biradicals (without an empirical factor) and disjoint biradicals (with an empirical factor), it does represent an improvement for calculating D values for the biradicals that do fall into these categories.

Results for all the biradicals studied are provided as supplementary material on the epoc website at http://www.wiley.com/epoc.

Acknowledgements

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