SPIN–ORBIT COUPLING IN BIRADICALS. 4. ZERO-FIELD SPLITTING IN TRIPLET NITRENES, PHOSPHINIDENES, AND ARSINIDENES[+]

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Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.

The spin dipole–spin dipole and spin–orbit coupling contributions to the zero-field splitting parameter D of CH_3–N, CH_3–P, CH_3–As, SiH_3–N, SiH_3–P, and SiH_3–As have been calculated from CAS(12,11)/cc-pVTZ wave functions and the Breit–Pauli Hamiltonian at T_1 B3LYP/cc-pVTZ optimized geometries. The spin–orbit coupling contributions represent a minor correction for the nitrenes, and bring the value computed for methylnitrene from 1.66 to 1.84 cm^{-1}, in good agreement with experiment (1.72 cm^{-1}). They dominate the spin–spin terms by an order of magnitude in phosphinidenes and by more than two orders of magnitude for arsinidenes. The properties of all these perfect axial biradicals follow expectations based on the simple algebraic 2-in-2 model of biradical structure.

Keywords: Radicals; Spin–orbit coupling; EPR spectroscopy; CASSCF; Triplet states; Wave functions; *Ab initio* calculations.

Reactive intermediates are commonly characterized under conditions of isolation in matrices and glasses. Triplet species are particularly conveniently and sensitively detected by electron paramagnetic resonance spectroscopy (EPR) and characterized by the zero-field splitting (zfs) parameters D and E. In organic molecules, these quantities are usually thought to be dictated nearly exclusively by the spin dipole–spin dipole (SS) interaction

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term in the molecular Hamiltonian operator, and are taken as a measure of the average separation of the two unpaired electrons, and of the deviation of their distribution from cylindrical symmetry, respectively. They have been used successfully as one of the criteria of the correctness of structural assignments.

As interest in organic reactive intermediates gradually extends to those including one or more atoms from the lower rows of the periodic table, the neglect of the role played by spin–orbit coupling (SOC), the other term of the Hamiltonian that contributes to zero-field splitting, becomes problematic. The degree to which the presence of a heavy atom in the molecule affects the zfs parameters is a sensitive function of molecular structure, and it is not always obvious when the zfs parameters lose their simple relation to molecular structure through the sole intermediacy of the distribution of the unpaired spins. In the case of triplet carbenes, whose zfs is dominated by SS even though the T_1–S_0 SOC is among the larger known in organic molecules (≈ 12 cm^{-1} in CH_2), it is sufficient to replace the divalent carbon by a silicon atom for SOC to become a more than equal partner in determining the zfs parameters[2]. This is understandable, since essentially all of the SOC are contributed by this carbon atom. The very recent experimental identification of a triplet ground state silylene[3] actually benefited from the published prediction of an unusually large value of D. Further increase in SOC is expected upon going further down the Periodic Table[4].

Presently, we report a similar prediction for another important class of organic reaction intermediates, nitrenes and their heavier analogues: CH_3–N, CH_3–P, CH_3–As, SiH_3–N, SiH_3–P, and SiH_3–As. Whereas the spectroscopy of numerous nitrenes has received considerable attention for decades[5,6], only mesitylphosphinidene[7] and very recently, silylphosphinidene[8], have been directly observed. Arsinidenes and heavier congeners are virtually unknown. The availability of predictions for the zfs parameter D could be helpful in a search for the spectroscopic signals of new intermediates of these types.

Carbenes and silylenes can be viewed as 1,1-biradicaloids, and would be perfect[9] 1,1-biradicals only when linear at the divalent atom, since only then would they have two exactly degenerate approximately non-bonding orbitals, half-filled in the ground state. In contrast, nitrenes and their analogues are perfect biradicals of the axial type[9] as long as the substituent on nitrogen has a threefold or higher axis of symmetry. In the simple "2-in-2" (or "3 × 3") algebraic model of biradical electronic structure, perfect axial biradicals have a triplet ground state T_1, a degenerate lowest singlet S_0S_1,

equal energy gaps between T_1 and the S_0S_1 pair and between the latter and a non-degenerate first excited singlet S_2, no SOC between T_1 and S_0S_1, and strong SOC between T_1 and S_2 (ref.[10]). Indeed, among triplet ground state organic molecules, nitrenes stand out as having a particularly large triplet–singlet energy splitting.

COMPUTATIONAL

Molecular geometries were optimized for the triplet ground state at the B3LYP/cc-pVTZ level using the Gaussian 03 program[11]. At these geometries state-specific CASSCF(12,11) wave functions were computed for three lowest triplet states (a nondegenerate T_1 state of A_2 symmetry, and degenerate pair of T_2 and T_3 states of E symmetry) and five singlet states (S_0 and S_1 degenerate pair of E symmetry, S_2 state of A_1 symmetry, and a pair of S_4 and S_5 states of E symmetry). The wave functions were generated by the MOLCAS 5.4 program[12] with an added interface to our program[13] for the calculation of SO and SS matrix elements using the full (including both, one- and two-electron operators) Breit–Pauli Hamiltonian and of the D and E zfs parameters employing first-order quasi-degenerate perturbation theory. The possible need for inclusion of higher singlet and triplet states in the zero-order basis was tested using the first ten singlet and six triplet states, which occur in the same energy region, using state-averaged wave functions. Only the states included in the above state-specific calculations were found to be important. Because the CASSCF calculations do not provide accurate enough excitation energies, which are needed in the quasi-degenerate perturbation treatment, all the energies were evaluated using multi-state CASPT2 theory including the lowest three states for triplets and five states for singlets.

RESULTS

The ground states of all the species examined, MH_3–X (M = C, Si; X = N, P, As), are triplets by substantial margins. The optimized (B3LYP/cc-pVTZ) geometries are of C_{3v} symmetry, and the zfs parameter E therefore vanishes. The geometries are listed in Table I.

In Table II, we collect the excitation energies of the lowest few excited states. The nature of the lowest triplet T_1 and of the lowest three singlets S_0, S_1, and S_2 is exactly that expected from the simple 2-in-2 model of electronic structure of ditopic biradicals[9], with the two non-bonding p orbitals on the monovalent atom playing the role of the half-filed shell and with

the S_0, S_1 state pair degenerate. The next higher triplet is also degenerate (T_2T_3) and is reached from T_1 by excitation of an electron from the mostly s-character lone pair orbital on the monovalent atom into the p orbitals of its half-filled shell.

Table III lists two values of the zfs parameter D. D_{SS} is calculated from the SS interaction alone, whereas D_{SS+SOC} includes both the SS and the SOC contributions. The magnitude of the SOC matrix element $SOC(T_1,S_2)$ connecting the T_1 and S_2 states, and its decomposition[2] into the term due to the monovalent atom X (N, P, or As) and that due to the substituent atom M (C or Si), are shown as well. The SOC matrix elements connecting the T_1 state with the other three states are listed as well. The matrix element $SOC(T_1,S_0S_1)$ is negligible.

The contribution of SOC to the values of the zfs parameter D is obtained using first-order quasi-degenerate perturbation theory. It is clearly only approximate since only the lowest singlet and triplet states have been included in the basis in which the matrix of the relativistic Breit–Pauli Hamiltonian has been evaluated and diagonalized. The agreement found below for the one species for which an experimental value is available, methylnitrene, suggests that the computed values are meaningful, but it is clear that they cannot be highly accurate. This is particularly true for the heavier congeners in the series, for which the SOC term dominates. It is also possible that for arsinidenes the Breit–Pauli spin–orbit Hamiltonian is inadequate, that the neglected scalar relativistic corrections could affect the energy of the unperturbed states significantly, and that SOC no longer is a minor perturbation relative to electron–electron repulsion. This would be even more likely the case for stibinidenes and bismuthinidenes, and we have therefore not attempted to perform calculations for them.

TABLE I
B3LYP/cc-pVTZ optimized geometries (in Å and °) of A_2 symmetry T_1 state of MH_3–X (M = C, Si; X = N, P, As)[a]

X	R_{CX}	R_{CH}	α_{HCX}	R_{SiX}	R_{SiH}	α_{HSiX}
N	1.409	1.100	111.0	1.796	1.485	108.2
P	1.852	1.092	110.7	2.266	1.487	110.2
As	1.982	1.090	110.0	2.379	1.487	110.3

[a] Optimized symmetry: C_{3v}.

TABLE II
CASSCF(12,11)/cc-pVTZ and MS-CASPT2 total energies (in a.u.) and vertical excitation energies relative to T_1 state (in kcal/mol) of $MH_3–X$ (M = C, Si; X = N, P, As)

Molecule	State	Symmetry	E(CAS)	ΔE(CAS)	E(PT2)	ΔE(PT2)
$CH_3–N$	T_1	A_2	–94.12380		–94.39321	
	T_2,T_3	E	–93.96510	99.6	–94.24119	95.4
	S_0,S_1	E	–94.05640	42.3	–94.33949	33.7
	S_2	A_1	–94.02640	61.1	–94.30330	56.4
	S_3,S_4	E	–93.89970	140.6	–94.17950	134.1
$CH_3–P$	T_1	A_2	–380.43336		–380.70951	
	T_2,T_3	E	–380.28627	92.3	–380.56854	88.5
	S_0,S_1	E	–380.38570	29.9	–380.67380	22.4
	S_2	A_1	–380.36416	43.4	–380.64370	41.3
	S_3,S_4	E	–380.24886	115.8	–380.53120	111.9
$CH_3–As$	T_1	A_2	–2273.94325		–2274.28565	
	T_2,T_3	E	–2273.80177	88.8	–2274.14870	85.9
	S_0,S_1	E	–2273.89774	28.6	–2274.25060	22.0
	S_2	A_1	–2273.87501	42.8	–2274.22014	41.1
	S_3,S_4	E	–2273.77177	107.6	–2274.11897	104.6
$SiH_3–N$	T_1	A_2	–345.15982		–345.44086	
	T_2,T_3	E	–345.09336	41.7	–345.36839	45.5
	S_0,S_1	E	–345.09564	40.3	–345.39082	31.4
	S_2	A_1	–345.07127	55.6	–345.36044	50.5
	S_3,S_4	E	–345.03181	80.3	–345.31617	78.2
$SiH_3–P$	T_1	A_2	–631.47406		–631.76695	
	T_2,T_3	E	–631.37887	59.7	–631.67847	55.5
	S_0,S_1	E	–631.42445	31.1	–631.73250	21.6
	S_2	A_1	–631.40363	44.2	–631.70409	39.4
	S_3,S_4	E	–631.34686	79.8	–631.64642	75.6
$SiH_3–As$	T_1	A_2	–2524.98605		–2525.34656	
	T_2,T_3	E	–2524.89036	60.0	–2525.25661	56.4
	S_0,S_1	E	–2524.94010	28.8	–2525.31305	21.0
	S_2	A_1	–2524.91834	42.5	–2525.28470	38.8
	S_3,S_4	E	–2524.86080	78.6	–2525.22647	75.4

DISCUSSION

There is nothing unusual about the optimized geometries of the triplet ground states (Table I). The optimization at the CASSCF(12,11)/cc-pVTZ level, calculated for CH_3–N for comparison, predicted slightly longer bond distances (C–N by 2 pm, C–H by 1 pm). The bond angles are practically identical at both levels of calculation.

The computed vertical excitation energies of the three singlet states, which are described by the simple 2-in-2 algebraic model of biradical electronic structure (Table II), reproduce quite well the equality of the T_1–S_0S_1 and S_0S_1–S_2 energy gaps anticipated from this model, and their magnitudes are quite reasonable. Comparison with experimental excitation energies is available only for CH_3–N. Its adiabatic T_1–S_0S_1 excitation energy has been determined by photoelectron spectroscopy[14] as 31.2 kcal/mol, to be compared with a vertical excitation energy of 33.7 kcal/mol listed in Table II, and its adiabatic T_1–T_2T_3 excitation energy[6] is 91 kcal/mol, compared with the presently calculated vertical energy of 95.4 kcal/mol. The geometry of the S_0 state has C_s symmetry due to a Jahn–Teller distortion, but differs only slightly from the T_1 geometry. For geometries and energies calculated at the CASSCF(12,11) level, it lies by 1.4 kcal/mol below the vertical excitation energy. Using this value, the estimate for the adiabatic excitation energy is 32.3 kcal/mol, in good agreement with the experimental value.

TABLE III
Zfs parameter D (in cm^{-1}) and SOC (in cm^{-1}) in MH_3–X (M = C, Si; X = N, P, As)

X	D_{SS}	D_{SS+SOC}	SOC_z (T_1,S_2)	$SOC_{x,y}$ (T_1,T_2T_3)	$SOC_{x,y}$ (T_1,S_0S_1)	$SOC_{x,y}$ (T_1,S_3S_4)	SOC_X (T_1,S_2)	SOC_M (T_1,S_2)
				H_3C–X				
N	1.66	1.84	62.70	39.94	0.48	36.48	98.6%	1.3%
P	0.36	3.46	218.39	118.10	0.84	123.20	99.5%	0.4%
As	0.26	86.49	1153.29	601.44	2.94	633.66	99.9%	0.1%
				H_3Si–X				
N	1.52	1.67	54.94	35.42	0.46	32.41	99.7%	0.2%
P	0.35	3.18	206.40	117.15	1.20	115.77	99.9%	0.1%
As	0.25	81.69	1105.41	617.45	4.25	631.56	100%	0%

For CH_3–P, the presently computed vertical T_1–S_0S_1 excitation energy of 28.9 kcal/mol can be compared with the previously calculated adiabatic values of 26 (ref.[15]) and 33 kcal/mol (ref.[16]).

We have not found much information on prior calculations of SOC in nitrenes other than a study of phenylnitrenes[17], and nothing on their heavier analogues. Our results for the SOC matrix elements (Table III) agree perfectly with expectations based on the algebraic 2-in-2 model: the T_1,S_0S_1 element is negligible and the T_1,S_2 element is large. In order to account for all five states calculated at relatively low energies, however, nitrene would have to be viewed as a tritopic rather than a bitopic biradical, *i.e.*, the sigma-symmetry lone pair orbital on the nitrogen atom would have to be added to the active space. As anticipated, the size of the SOC matrix elements increases rapidly with the atomic number of the monovalent atom in the molecule, which is responsible for the bulk of the computed *SOC* value.

The values of the zfs parameter *D* obtained from the SS term alone are relatively large for nitrenes and drop dramatically upon going down in the periodic table, as would be expected from the increasing size of the atomic orbitals. The values computed for the silyl derivatives are only very slightly smaller than those for the methyl derivatives, suggesting minimal delocalization of the unpaired electrons from the monovalent atom to the substituent. In the only case for which experimental data are available, methylnitrene, the SS-only value of *D*, 1.66 cm^{-1}, is in agreement with 1.720 cm^{-1}, which is the currently accepted experimental value, reached after some initial confusion[18].

The full *D* values of nitrenes obtained upon consideration of SOC as well as SS are similar to their SS-only values. The 1.84 cm^{-1} value for methylnitrene exceeds the experimental value by 7%. The good agreement suggests that the use of only a few first terms in the perturbation expression for the SOC contribution is acceptable in this case. Its importance should not be overestimated, however, since for nitrenes the SOC contribution is such a minor correction to the SS value that even if it were off by 10 or 20%, the overall agreement would still be similar. We believe that the observed 7% discrepancy in the *D* value is largely due to an overestimated SS-only contribution, and that this deficiency is probably due to missing dynamic electron correlation in the triplet CASSCF wave function[2].

As the atomic number of the monovalent atom grows, the SOC-induced increase in the computed *D* value becomes quite dramatic. In the phosphinidenes (phosphanylidenes), the SOC contribution exceeds the SS contribution by an order of magnitude, and in the arsinidenes (arsanylidenes), by more than two orders of magnitude, such that it is unnecessary to even cal-

culate the SS value at all. The predicted values for the phosphinidenes will presumably be useful in the search for their presently unknown EPR spectra. The value reported[7] for mesitylphosphinidene, 3.521 cm^{-1}, was obtained under the assumption $E = 0$, and is similar to those we calculate for methylphosphinidene and silylphosphinidene (Table III). The predicted values for the arsinidenes, although undoubtedly less accurate, make it clear that ordinary EPR instruments will not be very useful for their study.

The presence of silicon atom in the silyl substituent on the nitrene makes little difference for the computed D value. This is reasonable considering that 98.6% of the SOC matrix element originates on the nitrogen atom and only 1.4% on the substituent. Nitrene D values are known to be rather insensitive to the nature of a saturated substituent on the nitrogen atom; for instance, the replacement of the methyl by a trifluoromethyl group changes D from 1.720 to 1.736 cm^{-1} (ref.[18]). Overall, the results for nitrenes support the common belief that for organic molecules devoid of heavy atoms the SS contribution to D strongly dominates.

Also in the heavier congeners, the substitution of the methyl by a silyl group makes little difference, for similar reasons.

CONCLUSION

Both the state energy spacing and the SOC properties of methyl and silyl nitrenes, phosphinidenes, and arsinidenes follow expectations based on the algebraic 2-in-2 model. The zfs parameter D of methylnitrene has been calculated in a good agreement with the experimental value when the small SOC contribution was added to the dominant SS contribution. The predicted values of this parameter for phosphinidenes should be helpful for experimental efforts at their observation, and the values calculated for arsinidenes make it clear that these species will not be observable by standard EPR spectroscopy.

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