

## Magnetic circular dichroism of cyclic $\pi$ -electron systems. 29. Bicyclic phospholium and arsolium cations with phosphorus-sulfur, arsenic-sulfur, phosphorus-nitrogen, and arsenic-nitrogen $\pi$ bonding

B. W. Royan, N. Burford, J. Waluk, and Josef Michl

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removed. Evaporation of this Et<sub>2</sub>O clear solution to ca. 5 mL and cooling afforded a yellow product (**4a**), which was filtered and air-dried (0.34 g, 63% yield).

**5a** (70% yield) and **6a** (76% yield) were prepared similarly.

**Bis(μ-bromo)bis(5-(pentafluorophenyl)-1-3-η<sup>3</sup>-cyclohexenyl)dipalladium(II) (8a). Method A: From 1.** To a suspension of AgClO<sub>4</sub> (0.22 g, 1.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) were added 1,4-cyclohexadiene (0.1 mL, 1.06 mmol) and **1** (0.716 g, 0.53 mmol). The mixture was stirred at room temperature for 8 h, and the resulting precipitate (AgBr) was filtered. Evaporation of the solution to ca. 10 mL led to a yellow product (**8a**), which was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub>, and air-dried (0.25 g, 55% yield). The remaining solution was evaporated to dryness, and EtOH (20 mL) was added, affording an additional amount of **8a** which was filtered, washed with EtOH, and air dried (0.15 g), total yield 87%.

**3a** (85% yield) and **7a** (88% yield) were prepared similarly.

**Method B: From 2.** To a solution of **2** (0.2 g, 0.46 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added 1,4-cyclohexadiene (0.04 mL, 0.46 mmol). The mixture was stirred for 5 min. The yellow solution was evaporated, and *n*-hexane (5 mL) was added. A yellow product (**8a**) was obtained, which was filtered and air-dried (0.18 g, 90% yield).

**3a-7a** were also obtained by this same procedure in excellent yields (85-90%).

**(4-(Pentafluorophenyl)-1-3-η<sup>3</sup>-butenyl)(2,4-pentanedionato)palladium(II) (3b).** To a solution of **3a** (0.1 g, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (ca. 10 mL) was added Tl(acac) (0.075 g, 0.24 mmol). A white precipitate appeared immediately. The suspension was stirred for 15 min, and the precipitate was filtered off; the colorless solution obtained was evaporated to dryness, and *n*-hexane was added. A white product (**3b**) was obtained, filtered, and air-dried (0.07 g, 70% yield).

**4b** (60% yield), **7b** (51% yield), and **8b** (55% yield) were prepared similarly. **3b**, **7b**, and **8b** were stored at -20 °C because they decompose slowly at room temperature.

**Preparation of trans-PhCH=CH(C<sub>6</sub>F<sub>5</sub>) (9).** To a suspension of AgClO<sub>4</sub> (0.076 g, 0.366 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added styrene (0.042 mL, 0.366 mmol) and **1** (0.247 g, 0.183 mmol). During the reaction a Pd mirror appeared. After the mixture was stirred for 6 h, activated charcoal was added, and the suspension was filtered off. The solution obtained was evaporated to ca. 1 mL and cooled, affording white needles of **9** in 45% yield; <sup>19</sup>F NMR (200 MHz, CDCl<sub>3</sub>) δ -143.7 (m, F<sub>ortho</sub>), -157.5 (t, F<sub>para</sub>), -163.9

(m, F<sub>meta</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 6.98 (d, 2 H, *J* = 16.8 Hz), 7.43 (d, 2 H), 7.55-7.35 (m, Ph).

**Safety Note.** Although we have not had any problems using perchlorate salts, it is well-known that they are potentially explosive. Thus, *great caution* should be exercised when handling these materials.

**X-ray Structure Determination of 7a.** Crystals of **8a** suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. Crystal data and details of data collection and structure solution and refinement are collected in Table VII. An empirical absorption correction was applied.<sup>40</sup>

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**Registry No.** **1**, 124351-22-0; **2**, 125475-73-2; **3a**, 125494-79-3; **3b**, 125475-74-3; **4a**, 125494-80-6; **4b**, 125475-75-4; **5a**, 125494-81-7; **6a**, 125475-76-5; **7a**, 125475-77-6; **7b**, 125475-78-7; **8a**, 125475-79-8; **8b**, 125475-80-1; **9**, 19292-25-2; Tl(acac), 15525-62-9; 1,3-butadiene, 106-99-0; 1,4-diphenylbutadiene, 886-65-7; 2,4-hexadiene, 592-46-1; 1,3-cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; styrene, 100-42-5.

**Supplementary Material Available:** Tables of thermal anisotropic parameters and hydrogen coordinates, atomic coordinates, bond distances and angles, least-squares planes and dihedral angles, ring puckering coordinates, asymmetry parameters, and torsion angles (7 pages); a listing of structure factors (9 pages). Ordering information is given on any current masthead page.

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## Magnetic Circular Dichroism of Cyclic π-Electron Systems. 29.<sup>1</sup> Bicyclic Phospholium and Arsolium Cations with P-S, As-S, P-N, and As-N pπ-Bonding

B. W. Royan,<sup>2a</sup> N. Burford,<sup>2a</sup> J. Waluk,<sup>2b,c</sup> and J. Michl<sup>\*,2b</sup>

Center for Structure and Reactivity, Department of Chemistry,  
The University of Texas at Austin, Austin, Texas 78712-1167,  
and Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

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Electronic absorption and magnetic circular dichroism are reported for five bicyclic heterocycles derived from the phospholium and arsolium cations containing P-S, P-N, As-S, and As-N bonds. The spectra are analyzed in terms of the perimeter model and semiempirical calculations and are perfectly compatible with a delocalized aromatic π-electron system with pπ-bonding over the heterocyclic moiety.

### Introduction

We have recently reported the synthesis of cationic heteronaphthalenic systems, which contain the first ex-

amples of pπ-bonding between sulfur and the heavier elements of group 15.<sup>3-7</sup> Spectroscopic (NMR, IR, and mass

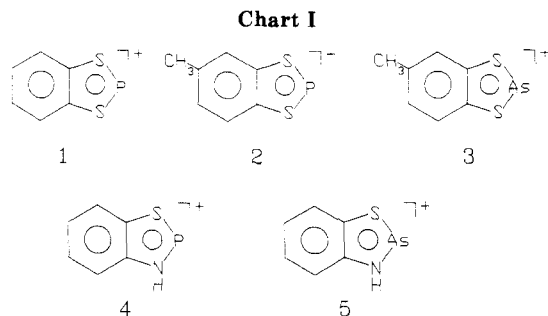
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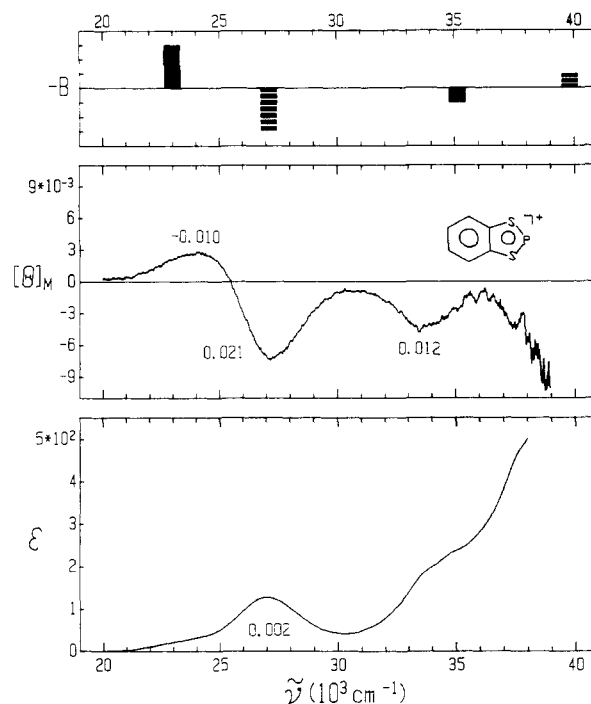
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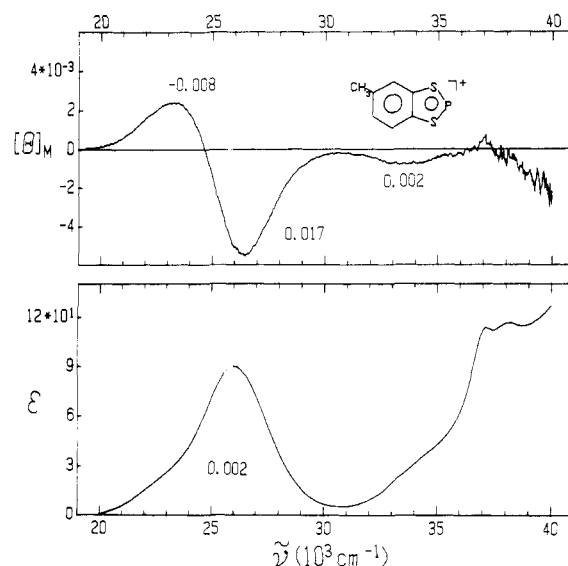
spectroscopy) characterization of a number of derivatives indicates an effective delocalization of the positive charge, and structural studies reveal planar frameworks with short heterocyclic bonds, consistent with a 10- $\pi$ -electron system. As a direct probe into the delocalized Hückel nature of these systems, we now report the magnetic circular dichroism (MCD) spectra of the 1,3,2-benzodithiaphospholium (1), 5-methyl-1,3,2-benzodithiaphospholium (2), 5-methyl-1,3,2-benzodithiarsolium (3), 1,3,2-benzothiazaphospholium (4), and 1,3,2-benzothiazarsolium (5) cations (Chart I) and their interpretation.

MCD spectra of many delocalized  $\pi$ -electron structures derived from a  $(4N + 2)$ -electron perimeter have been successfully interpreted in terms of the perimeter model.<sup>8,9</sup> The signs of MCD  $B$  terms are readily accounted for by the qualitative analysis of energy splittings of the frontier  $\pi$  orbitals. When the characteristics of the perturbing heteroatoms or substituents are known (specifically, their electronegativities and resonance integrals), the  $B$  terms can be predicted. Conversely, a measurement of the  $B$  terms provides information on these characteristics where they may be less well established. For instance, an MCD study of phosphabenzene, arsabenzene, and stibabenzene<sup>10</sup> showed that  $\pi$ -orbital electronegativities of phosphorus, arsenic, and antimony are higher than that of carbon, somewhat contrary to intuition but in agreement with the tabulated values of atomic properties.

According to perimeter theory,<sup>8,9</sup> there are two contributions to the MCD  $B$  terms. The first are the so-called  $\mu^-$  contributions, which are always present, are relatively small, and have signs largely independent of molecular structure. The others,  $\mu^+$  contributions, are usually much larger and appear when the energy splitting between the highest occupied molecular  $\pi$  orbitals ( $\Delta\text{HOMO}$ ) differs from that between lowest unoccupied  $\pi$  orbitals ( $\Delta\text{LUMO}$ ) derived from the frontier orbitals of the perimeter. When the  $\mu^+$  contribution dominates, the theory predicts a +, -, + sequence of  $B$  terms for the lowest three  $\pi\pi^*$  states for  $\Delta\text{HOMO} > \Delta\text{LUMO}$ . The opposite sequence, -, +, -, is expected for  $\Delta\text{HOMO} < \Delta\text{LUMO}$ . When  $\Delta\text{HOMO} = \Delta\text{LUMO}$ , the  $\mu^+$  contributions vanish and  $\mu^-$  contributions are expected to dictate the MCD signs. Since an inequality of  $\Delta\text{HOMO}$  and  $\Delta\text{LUMO}$  can be induced even by quite weak perturbations (e.g. methyl substitution), MCD chromophores with  $\Delta\text{HOMO} \approx \Delta\text{LUMO}$  have been labeled soft. If  $\Delta\text{HOMO}$  and  $\Delta\text{LUMO}$  are substantially different, the substituent will in most cases not be able to change the sign of  $\Delta\text{HOMO} - \Delta\text{LUMO}$  and, thus, the signs of the  $B$  terms. Such chromophores are called "positive-



**Figure 1.** The 1,3,2-benzodithiaphospholium cation ( $\text{CH}_2\text{Cl}_2$ , 293 K): (bottom) absorption spectrum (oscillator strength given); (center) MCD spectrum (magnetically induced molar ellipticity in units of  $\text{deg G}^{-1} \text{m}^{-1} \text{M}^{-1}$ ,  $B$  terms in units of  $10^{-3} \beta_e \text{D}^2/\text{cm}^{-1}$ ); (top) results of PPP calculations, with solid bars for transitions polarized vertically and broken bars for those polarized horizontally with respect to formula 1 (the three different heights of the bars correspond to  $|B| < 1$ ,  $1 < |B| < 5$ , and  $|B| > 5$ , respectively).



**Figure 2.** The 5-methyl-1,3,2-benzodithiaphospholium cation ( $\text{CH}_2\text{Cl}_2$ , 293 K; see caption to Figure 1).

hard" ( $\Delta\text{HOMO} > \Delta\text{LUMO}$ ) or "negative-hard" ( $\Delta\text{HOMO} < \Delta\text{LUMO}$ ).

We now show that the MCD spectra of 1-5 can be satisfactorily analyzed by the perimeter model. All compounds reveal the same MCD pattern, characteristic of so-called "negative-hard" chromophores.<sup>9</sup> The spectra also are in full agreement with predictions based on the  $\pi$ -electron PPP<sup>11</sup> and all-valence-electron INDO/S<sup>12</sup> calculations.

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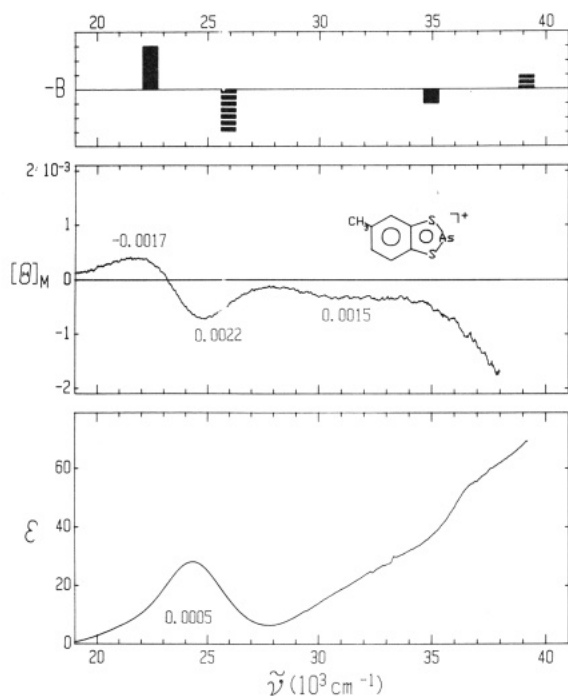
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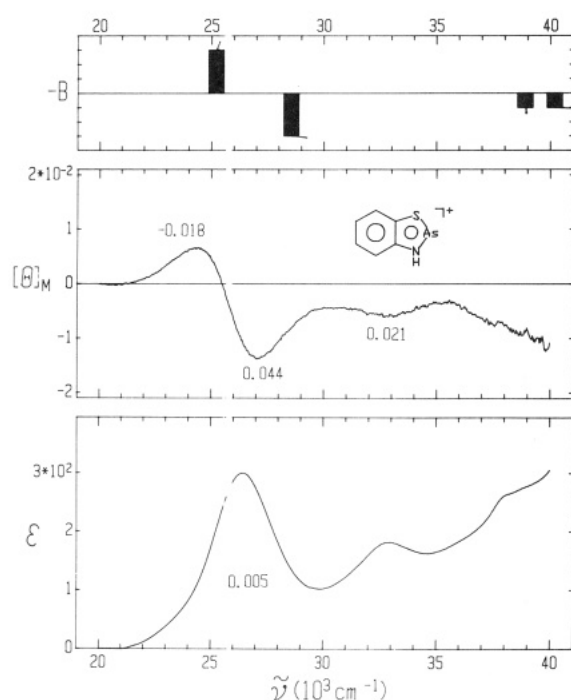
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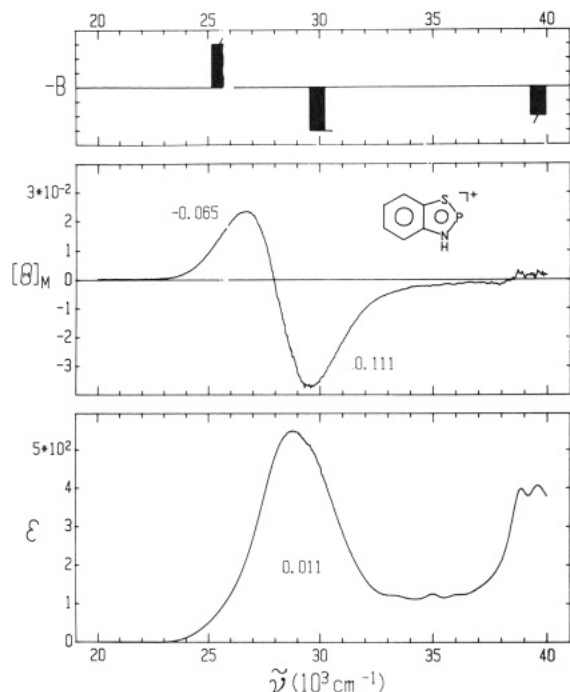
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**Figure 3.** The 5-methyl-1,3,2-benzodithiarsolium cation ( $\text{CH}_2\text{Cl}_2$ , 293 K; see caption to Figure 1). PPP calculations were done for the parent without the methyl group.



**Figure 5.** The 1,3,2-benzothiazarsolium cation ( $\text{CH}_2\text{Cl}_2$ , 293 K; see captions to Figures 1 and 4).



**Figure 4.** The 1,3,2-benzothiazaphospholium cation ( $\text{CH}_2\text{Cl}_2$ , 293 K; see caption to Figure 1). Polarization directions are shown with respect to the formula as drawn.

### Results and Discussion

The MCD and absorption spectra and the results of calculations are presented in Figures 1–5. The MCD spectra reveal the same pattern for all the compounds: a positive MCD signal for the first transition, corresponding to a negative  $B$  term, followed by two transitions with negative MCD signals (positive  $B$  terms). MCD spectra clearly show the presence of two transitions in the low-energy region. In the absorption spectrum, one of these can only be seen as a shoulder (1–3) or is not observed at all (4, 5). The differences in MCD intensities follow closely



**Figure 6.** Frontier  $\pi$  orbitals and their energy splittings calculated for 1 by the PPP method.

those in the absorption oscillator strengths. The latter are a strong function of the heteroatom.

It is evident from the spectra (–, + sequence of  $B$  terms for the first two excited states) that all compounds behave like negative-hard chromophores, implying  $\Delta\text{HOMO} < \Delta\text{LUMO}$ . This agrees with the results of calculations (Figure 6):  $\Delta\text{HOMO}$  is calculated to be about 1 eV and  $\Delta\text{LUMO}$  about 5 eV. The reason for the large imbalance is the very low energy of the first unoccupied  $\pi$  orbital (LUMO), largely localized on the five-membered ring. Its energy is so low that the first three excited states calculated by the PPP method are all described by configurations in which an electron is promoted into this orbital from the first, second, and third highest occupied  $\pi$  orbitals, respectively. The state that involves the third highest occupied MO is not described by the usual perimeter model and usually lies very high in energy. In the present case, however, a comparison of the experimental excitation energy, intensity, and MCD sign with the theoretical values suggests that it really corresponds to the third observed transition. Alternatively, the latter could be assigned to an  $n\pi^*$  state. INDO/S calculations performed for 1 predict such a transition about  $6000\text{ cm}^{-1}$  above  $S_1$  ( $\pi\pi^*$ ), also with a positive  $B$  term. However, this method frequently gives

energies too low for  $n\pi^*$  levels.

No matter what the origin of the  $S_3$  state,  $S_1$  and  $S_2$  can be unequivocally assigned as the  $L_1$  and  $L_2$  states of a  $\pi$ -electron perimeter, with the signs of  $B$  terms correctly predicted by theory. All the compounds investigated may thus be termed aromatic in the UV-spectroscopic sense.

The perimeter model also allows us to analyze changes in the magnitudes of  $B$  terms caused by varying the substituents. Two effects should be considered. First, inductive perturbations will stabilize the orbital energy if the substituent is electron-withdrawing (+I) and destabilize it if it is electron-donating (-I). This effect should be important for the lowest unoccupied and the second highest occupied orbitals for substitution in position 2 and for the highest occupied and the lowest unoccupied orbitals for substitution in positions 1 and 3 (Figure 6). Second, changes in resonance integrals will affect the lowest unoccupied orbital: the smaller the value of  $|\beta|$  for the 1-2 (2-3) bond, the more stabilized and less antibonding this orbital will be.

The MCD spectra show that the first effect is dominant in the present case. The replacement of phosphorus by the less electronegative arsenic significantly lowers the absolute values of the  $B$  terms of  $S_1$  and  $S_2$  transitions (cf. Figures 2 and 3 and Figures 4 and 5), which implies that  $|\Delta\text{HOMO} - \Delta\text{LUMO}|$  is larger in the phospholium cations, most probably because the lowest unoccupied orbital has lower energy than in arsolium derivatives. In agreement with this,<sup>9</sup> the oscillator strength of the L bands is also reduced. The opposite effect is observed upon replacement of sulfur by the NH group. Now, both the highest occupied and the lowest unoccupied orbitals should have lower energy in the NH than in sulfur derivatives, which makes  $|\Delta\text{HOMO} - \Delta\text{LUMO}|$  larger in the former.

Thus, simple arguments based upon predictions of orbital energy shifts in the first-order perturbation theory seem to account well for the trends in the electronic and

MCD spectra of these novel heterocycles. The results are in full agreement with expectations for a delocalized (aromatic)  $\pi$ -electron system with partial double bonds across the P-S, As-S, P-N, and As-N linkages.

### Experimental and Computational Details

All compounds were prepared as tetrachloroaluminates.<sup>3-7</sup> These salts are extremely air- and moisture-sensitive. The solids were handled in a nitrogen-filled drybox, and all glassware was rigorously dried before use. MCD and absorption spectra were measured in spectral grade methylene chloride at 293 K. The solvent was dried three times over  $\text{CaH}_2$  under a nitrogen atmosphere and was stored in an evacuated vessel over  $\text{CaH}_2$ .

Solids were placed in cells specially designed for absorption and MCD measurements. Solvent transfer was accomplished through standard vacuum line techniques. Attempts to obtain spectra over a greater spectral range with acetonitrile and *n*-heptane as solvents were unsuccessful due to reaction with the salts and insolubility, respectively.

MCD spectra were taken on a JASCO J-600 spectropolarimeter equipped with a 16-kG electromagnet by using procedures described earlier.<sup>1</sup> Absorption spectra were obtained on a Varian 2300 spectrophotometer.

Calculations were performed by the PPP method, with use of the experimental geometries of 1, 4, and 5. The following parameters were used (in eV): 11.42 ( $I_C$ ), 20.27 ( $I_S$ ), 11.05 ( $I_P$ ), 9.36 ( $I_{As}$ ), 23.13 ( $I_{NH}$ ), 0.58 ( $A_C$ ), 10.47 ( $A_S$ ), 1.53 ( $A_P$ ), 1.49 ( $A_{As}$ ), 9.1 ( $A_{NH}$ ), -2.318 ( $\beta_{CC}$ ,  $\beta_{CN}$ ), -1.62 ( $\beta_{CS}$ ), -1.4 ( $\beta_{SP}$ ,  $\beta_{NP}$ ), -1.2 ( $\beta_{SAs}$ ,  $\beta_{NAAs}$ ). All singly excited configurations were included in the CI procedure. For 1, an INDO/S calculation was also performed, with 100 lowest singly excited configurations as the CI basis.

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