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Stabilization of diazene in Fe(II)–sulfur model complexes relevant for nitrogenase activity. I. A new approach to the evaluation of intramolecular hydrogen bond energies

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Abstract. A key step in the biological nitrogen fixation problem is the transfer of protons and electrons onto inert molecular nitrogen. A first intermediate will then be diazene (diimide), N_2H_2, which is thermodynamically unstable with respect to dissociation into N_2 and H_2 in the gas phase. Thus, diazene must be stabilized such that the reduction of a complex binding an activated nitrogen becomes energetically feasible. A considerable contribution to this stabilization has been attributed to hydrogen bonds of the type N–H···S. We investigate the strength of these hydrogen bonds in two model compounds. Since the contribution of an intramolecular hydrogen bridge to the total binding energy of a molecule is not a well-defined concept, it is necessary to define a suitable descriptor for this quantity. We present a new approach of estimating hydrogen-bond energies from two-center shared-electron numbers obtained from density functional calculations. Our approach is particularly designed for highly complex systems such as transition-metal complexes with large coordination spheres.

Key words: Diazene complexes – Hydrogen bonding – Density functional calculations – Iron–sulfur complexes – Shared-electron numbers

1 Introduction

The nitrogenase-catalyzed reduction of molecular nitrogen to ammonia is one of the syntheses fundamental for life. The mild ambient conditions, i.e., standard temperature and pressure and, in particular, biological redox potentials (as opposed to the drastic conditions of the Haber–Bosch process), under which nature reduces inert N_2 molecules at the active site of this enzyme are a persistent challenge for chemists [1, 2]. However, up to now it has not yet been possible to find a model compound which catalyzes nitrogen reduction under nitrogenase-like conditions.

A giant step forward to solving the nitrogen fixation problem has been the X-ray structural characterization of FeMo nitrogenase and its active site, the FeMo cofactor (FeMoco) [3]. However, the turnover state of the enzyme and all key steps of the reduction process remain unclear. Thus, all chemical mechanisms which have been suggested for the nitrogenase catalyzed N_2 reduction so far remain largely speculative [4–7].

Hints for the solution of the problem may be deduced from studying model compounds. Quantum chemical calculations on such model compounds can be used to settle questions such as the energetic contribution of certain structural features of these complexes, which are not easily amenable to experiment. The structure of FeMoco allows one to construct a large diversity of model complexes that exhibit transition metals in a sulfur coordination sphere [8–12]. We focus on the extensive work on iron complexes with sulfur ligands that bind N_xH_y molecules which are potential intermediates in N_2 fixation [7, 13, 14]. Two of these model complexes are shown in Fig. 1. The role of hydrogen bonds between the N_xH_y species with thiolate and thioether functionalities of the model complex is the example which we study in this work. We aim at calculations which closely parallel the experimental work on model compounds, and thus include the full ligands in our calculations, as far as computationally feasible.

A major role in the mechanism has been attributed to hydrogen bonds of the type N–H···S [15, 16]. It has been estimated from empirical data that these hydrogen bonds contribute approximately 70 kJ/mol to the total stabilization of coordinated diazene, N_2H_2 [15]. The strength of these hydrogen–sulfur bonds is not directly accessible by experiment, since it is not an observable in the strict sense; however, several strategies can be

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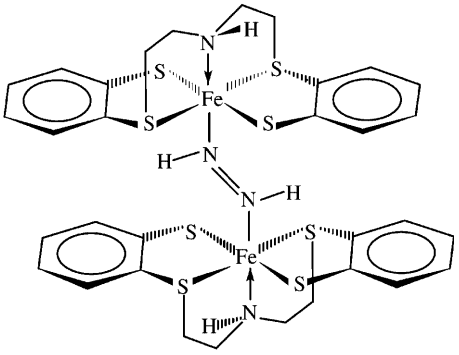
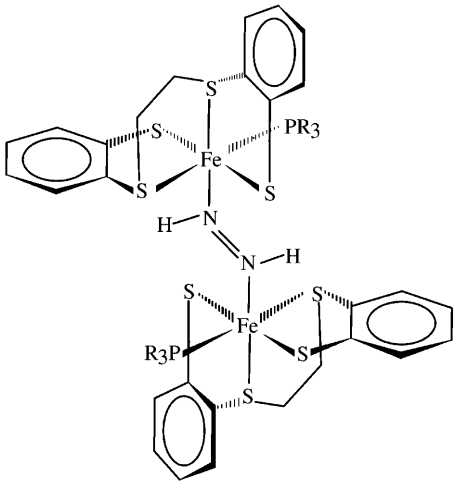


$[\mu\text{-}N_2H_2\{Fe(N_HS_4)\}_2]$



$[\mu\text{-}N_2H_2\{Fe(S_4)PR_3\}_2]$

Fig. 1. Dinuclear Fe(II)–S model complexes which coordinate diazene

devised and tested by quantum chemical means which are capable of assessing the importance of such structural features for the stabilization of the ligand. The present work deals with the development of a method for a sufficiently accurate estimation of the strength of these intramolecular hydrogen bonds, which, in particular, is applied to diazene model compounds.

Our approach is a parameterization of a linear relationship between two-center shared-electron numbers (SENs) (i.e., numbers of electrons belonging to both bonding partners) and hydrogen-bond energies obtained from the supermolecular approach. Its main advantage is that it can be evaluated readily once the one-electron wavefunctions, i.e., the molecular orbitals, are known. The method is applicable in many other areas where hydrogen bonding plays a dominant role [17–20].

The article is organized as follows: In the first section we discuss the problems which arise in estimating intramolecular hydrogen-bond energies and describe the approach developed in this work. We describe the parameterization of our SEN method by using reference data obtained from the calculation of interaction energies of molecules which are associated by intermolecular hydrogen bonds. We then assess the versatility of the method by application to three examples: the formic and acetic acid dimers and malonic acid. In order to explore the range of applicability of the new method we extend the study to diazene-coordinating iron(II)–sulfur compounds. For this purpose we estimate the hydrogen-bond energies with the SEN method and compare them to results from the calculations based on the total energy of the complex in various conformations of the diazene ligand. Details of the quantum mechanical treatment are given in the Appendix.

2 Strategies to extract the strength of hydrogen bonds from electronic structure

Hydrogen bonds are known to play an important role in different branches of science [21–26], particularly in proteins, metal clusters bound in enzymes or substrates coordinating to these clusters. The main quantum chemical approaches which are in use for calculating the binding energy of weakly interacting systems such as molecular fragments bound by hydrogen bridges are the supermolecular approach and intermolecular perturbation theory [27, 28].

The supermolecular approach treats the whole hydrogen-bonded complex as a single molecule. A binding energy unambiguously attributable to the hydrogen bridge can only be obtained from this approach if there are indeed no other interactions between the fragments, i.e., if the binding is solely attributable to the hydrogen bond. This is obviously only the case for separable complexes consisting of rigid molecules whose structure is not changed much after breaking the single hydrogen bond in question. However, in many cases of practical interest conformational changes have to be taken into account and the decomposition energy, i.e., the energy needed for decomposing the complex into its molecular fragments, is the sum of many different effects, so a hydrogen-bond energy cannot be extracted.

It should be clear after this discussion that the "hydrogen-bond energy" is, in general, not a physical observable in the sense that we have an unequivocal prescription of its measurement. Rather, our goal is to get an estimate of the amount of energy that a given structural motif, in our case a hydrogen bridge, contributes to the total energy of a complex. The contribution of a hydrogen bond to the stability of a compound is a small energy quantity of the order of several tens of kilojoules per mole, and the contribution of the weaker ones may well be of the order of the error of the quantum chemical method employed. From an optimistic viewpoint, this error in the calculation of bond dissociation energies of small compounds is expected to be of the order of 5 kJ/mol. We therefore aim at designing a method to extract the energetic contribution of a structural motif like a hydrogen bond from electronic-structure calculations with an error margin of about this size.

We propose two types of energetic descriptors for the contribution of an intramolecular hydrogen bond within a complex structure. The first uses only integral quantities

of the molecule, while the other makes use of orbital-based concepts and is settled in molecular orbital theory. In the former (supermolecular) description we try to estimate the hydrogen-bond energy from the energy difference of molecules featuring suitably chosen structural changes (i.e., dissociation, isomerization, rotation of a substructure), while the orbital-based description uses decomposition schemes of the total electronic density in terms of the molecular orbitals obtained from a Hartree–Fock or a density functional calculation. The latter method is similar in spirit to energy decompositions in terms of natural orbitals [29–31], but makes use of so-called modified atomic orbitals [32].

The energetic data which can be extracted from conformational changes may be of three kinds. The first approach is most obvious but applicable only to comparably few, small systems. In the case of two molecules interacting exclusively through a single hydrogen bond, the energy difference of this supermolecule and its two components is attributed to the interaction energy due to the hydrogen bond and is dubbed $E_{\mathrm{HA}}^{\mathrm{I}}$ in the following. We choose here to exclude the energy contribution from the conformational relaxation of the fragments when forming the complex, which is in line with current definitions of the complex interaction energy (page 1377 of ref. [28]).

As a second possibility, we could get an energy measure by breaking the hydrogen bond through changing an appropriate internal coordinate, for example, flipping the hydrogen atom by 180° so that a cisoid structure is transformed into its transoid analogue. The difference in energy between such isomers is another estimate for the hydrogen-bond energy, which we denote by $E_{\mathrm{HA}}^{\mathrm{iso}}$. We have to bear in mind that the isomerization itself leads to a nonnegligible energy contribution to be subtracted from the energy difference. Moreover, this definition can only be used if the hydrogen donor or acceptor parts of the supermolecule are themselves meaningful chemical structures such that their isomerization energies are well defined.

A third approach is offered by the calculation of a rotational barrier which incorporates the breaking of the hydrogen bond. Here we compare the structure exhibiting the hydrogen bond with a noninteracting structure taking into account that an energy due to the conformational change has to be subtracted, yielding $E_{\mathrm{HA}}^{\mathrm{R}}$. Again we must be able to find an estimate for this conformational energy which we could obtain from a rotational curve of a similar compound without exhibiting a hydrogen bond. Care also has to be taken in this case since the breaking of multiple bonds (e.g., bonds with double-bond character such as those stabilized through back donation) could lead to wrong approximations for the hydrogen-bond energy.

It turns out that all three methods are of limited use for highly complex systems, but they are useful to calibrate simpler and more easily accessible measures which are based on the molecular orbitals alone.

Qualitative interpretation of bond strengths often stipulates that the bond energy is correlated with the number of bond electrons represented in a Lewis structure. The charge density analysis by Davidson [33], Roby [34], Heinzmann and Ahlrichs [32] and Ehrhardt and Ahlrichs [35] provides two-center SENs which give an intuitive measure of the strength of a bond and have indeed been shown to provide a quantitative measure for the strength of a covalent bond [32, 35]. The authors of Refs. [32, 35] established a linear relationship between SENs and bond energies for covalent chemical bonds such as those in H_2 and Li_2. For this type of bonds one would expect to find SENs close to unity, although the bond energies differ largely. In the method of Ahlrichs and coworkers this is taken into account by choosing an appropriate center of energy for each diatomic species making use of the ionization energies of the constituent atoms.

There are hints that a similar linear relationship can also be established between hydrogen-bond energies and a population analysis based measure for the number of shared electrons in the hydrogen bond [36]. Our goal in the present work is to extend the scheme of Ahlrichs and coworkers to hydrogen-bond energies such that an energy value $E_{\mathrm{HA}}^{\mathrm{SEN}}$ can be assigned to a SEN in order to calculate, in particular, intramolecular hydrogen-bond energies.

3 The SEN method

The number of electrons shared by two atoms within a molecule, i.e., the two-center SEN, may be defined following Davidson [33] as

$$\sigma_{\mathrm{AB}} = N_{\mathrm{A}} + N_{\mathrm{B}} - n_{\mathrm{AB}} \ , \tag{1}$$

where n_{AB} is the number of electrons of atoms A and B under investigation in the system and N_X is calculated as

$$N_X = \mathrm{tr} D P_X \ , \tag{2}$$

with P_X being the projector onto the space of occupied self-consistent-field atomic orbitals of atom X and D being the molecular one-particle density operator.

By extending the idea of establishing a linear relationship between SENs and bond energies developed by Ahlrichs and coworkers for covalent bonds [32, 35] to hydrogen-bonding interaction, we propose to determine the energy contribution of a hydrogen bond between a hydrogen atom, H, and the acceptor atom, A, by means of the linear relationship

$$E_{\mathrm{HA}}^{\mathrm{SEN}} = \lambda \sigma_{\mathrm{HA}} \ . \tag{3}$$

Equation (3) relates the two-center SEN σ_{HA} and the hydrogen-bond energy. Note that we adopt the same center of energy for all hydrogen bonds. It is obvious that a "hydrogen-bond energy" depends on many variables such as the D–H···A angle (D denotes the hydrogen donor atom and A again the correponding acceptor), the H···A distance, polarizabilities, dipole moments, etc. [37–39]. All these dependencies will be mapped onto the single value of a two-center SEN σ_{HA}.

We determine the parameter λ of the linear relationship through linear regression to interaction energies obtained from density functional theory calculations on small molecule complexes. Hydrogen-bond energies $E_{\mathrm{HA}}^{\mathrm{I}}$ in these hydrogen-bonded complexes, which are connected via a single hydrogen bridge, can be

calculated accurately by means of the supermolecular approach.

Our test set represents typical hydrogen-bond energies of uncharged molecules. Although many of these complexes contain *trans*-diazene as the hydrogen donor, it will turn out in the next section that this will not affect the general applicability of the method. In fact, the demonstration of the applicability of the SEN method confirms nicely the underlying physical basis of the method.

Corrections for the basis-set superposition error were not taken into account. In a previous Hartree–Fock study of hydrogen-bond interactions [40] we found for basis sets of SV(P) quality, which do not have polarization functions at hydrogen atoms, that the basis-set superposition error is to a large extent canceled by the error introduced by the deficiency of the Hartree–Fock method to describe the contribution of electron correlation to the binding energy. Since a substantial part of the hydrogen-bond interaction is due to dispersion-like interactions we expect that a similar cancellation also takes place for density functional theory (DFT) calculations, which are not able to account for long-range dispersion.

Hydrogen-bond energies E^{I}_{HA} and the corresponding SEN generated to serve as the reference data are given in Table 1. These energies change substantially for different functionals and basis sets since structural optimizations have been done for each hydrogen-bonded dimer; however, it is not necessary to be at the minimum of the electronic potential-energy surface (PES) because for any structure on the PES the SEN σ_{HA} belongs to the corresponding hydrogen-bond energy in that structure. Therefore, we accept that our structure optimization leads to different local minima with different basis sets and functionals. λ as obtained from a linear regression is given in Table 2. Note that the variation of the λ values with functionals and basis sets is relatively small, since typical σ_{HA} are of the order of 0.01e. This demonstrates a satisfactory independence of the fit from the functional and basis set chosen: increasing the SEN by 0.01 leads to an increase of about 5 kJ/mol in the hydrogen-bond energy. For rough estimates one may use $\lambda = 5$ kJ/mol $\times$ 0.01e for functionals or basis sets not considered here.

We analyze our fit further by calculating the empirical standard deviation and test on the level of confidence according to Student's t distribution (Table 2): the standard deviation for "secondary data" is obtained by analyzing the difference of the computed value for the hydrogen-bond energy and the value obtained from Eq. (3) at the given SEN. This implies that the mean value should be zero. For the standard deviation we note that it is smaller than 3.5 kJ/mol – except in the case of the B3LYP/SV(P) calculation, where it is 4.7 kJ/mol. Thus our fit should be satisfactory within the error bounds we were heading for. Moreover, we find from the t statistic that the data points are described properly by the linear regression with greater than 99% confidence.

4 Validation of the SEN method: carboxylic acid dimers and malonic acid

As discussed earlier, it is possible to determine the energy of a hydrogen bridge by means of supermolecular

Table 1. Density functional theory hydrogen-bond energies E^{I}_{HA} (kJ/mol) and two-center shared-electron numbers σ_{HA} calculated on the basis of the supermolecular approach for some selected small uncharged systems. All results are given for 0K without zero-point energy correction

Complex	Method							
	BP86/RI				B3LYP			
	SV(P)		TZVP		SV(P)		TZVP	
	E^{I}_{HA}	σ_{HA}	E^{I}_{HA}	σ_{HA}	E^{I}_{HA}	σ_{HA}	E^{I}_{HA}	σ_{HA}
HSH···S(CH$_3$)$_2$	3.90	0.0133	2.80	0.0130	4.98	0.0092	3.41	0.0085
*t*N$_2$H$_2$···SH(CH$_3$)	4.32	0.0133	2.80	0.0138	5.75	0.0112	3.75	0.0113
*t*N$_2$H$_2$···S(CH$_3$)$_2$	5.85	0.0138	4.40	0.0141	7.30	0.0117	5.39	0.0144
*t*N$_2$H$_2$···SPhH	8.02	0.0191	5.17	0.0183	9.27	0.0137	5.65	0.0119
*t*N$_2$H$_2$···SPh(CH$_3$)	8.54	0.0235	5.74	0.0211	10.4	0.0176	6.65	0.0169
*t*N$_2$H$_2$···PH$_3$	8.96	0.0182	5.67	0.0239	9.96	0.0131	6.47	0.0165
*t*N$_2$H$_2$···SH$_2$	9.90	0.0209	5.83	0.0240	11.0	0.0192	6.53	0.0156
H$_3$N···S(CH$_3$)$_2$	10.0	0.0182	2.82	0.0068	5.08	0.0061	3.74	0.0060
HSH···SH(CH$_3$)	12.2	0.0362	8.45	0.0364	11.4	0.0213	7.32	0.0239
*t*N$_2$H$_2$···FCH$_3$	12.2	0.0129	5.02	0.0072	12.7	0.0084	7.70	0.0076
*t*N$_2$H$_2$···P(CH$_3$)$_3$	16.0	0.0372	11.7	0.0373	17.1	0.0298	12.0	0.0271
*t*N$_2$H$_2$···O(CH$_3$)$_2$	17.4	0.0252	12.7	0.0242	20.2	0.0215	15.2	0.0242
HSH···OH$_2$	17.4	0.0340	10.5	0.0248	17.9	0.0233	11.2	0.0177
*t*N$_2$H$_2$···OH(CH$_3$)	19.2	0.0300	13.2	0.0254	21.8	0.0256	15.4	0.0212
*t*N$_2$H$_2$···OH$_2$	24.0	0.0358	14.1	0.0244	25.0	0.0297	15.4	0.0191
*t*N$_2$H$_2$···N(CH$_3$)$_3$	24.4	0.0542	17.8	0.0477	25.0	0.0424	18.6	0.0377
HOH···OH$_2$	28.3	0.0475	19.7	0.0338	30.5	0.0419	21.6	0.0285
*t*N$_2$H$_2$···NH$_3$	29.6	0.0616	21.0	0.0480	29.9	0.0480	21.4	0.0374
HOH···S(CH$_3$)$_2$	31.3	0.0585	20.1	0.0673	31.3	0.0428	19.8	0.0500
HOH···NH$_3$	40.5	0.0878	32.3	0.0745	40.2	0.0770	31.7	0.0606

Table 2. Results for least-squares fits $E_{HA}^{SEN} = \lambda\sigma_{HA}$ according to Eq. (3). r is the correlation coefficient, t the result of Student's t statistic, reference values: $t(1\%,19) = 2.86$ and $t(0.1\%,19) = 3.88$ [59], and σ is the empirical standard deviation

	Method			
	BP86/RI		B3LYP	
	SV(P)	TZVP	SV(P)	TZVP
λ [kJ/(mol e)]	495	380	637	514
r	0.95	0.91	0.94	0.91
t	3.70	3.87	3.40	3.66
σ (kJ/mol)	3.4	3.5	4.7	3.4

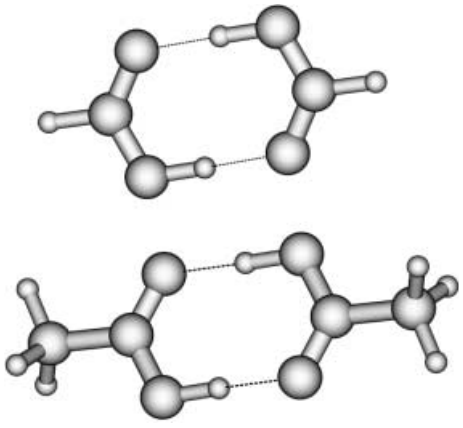


Fig. 2. Hydrogen bonding in the formic acid dimer $(COOH)_2$ (*top*) and the acetic acid dimer $(H_3C–COOH)_2$ (*bottom*)

methods, when it is practically the only mechanism for binding between the interacting fragments. This is to a good approximation the case in carboxylic acid dimers, and we therefore calculated the interaction energies for formic acid dimer and acetic acid dimer (Fig. 2) in order to validate the SEN method. Carboxylic acids form dimers in the gas phase with hydrogen-bond energies which are estimated to be in the range 25–30 kJ/mol per hydrogen bond (page 76 of ref. [41]). Previous calculations for the formic acid dimer carried out in our laboratory [40] have established a dissociation energy of 60–70 kJ/mol which after zero-point energy corrections compares well with the measured enthalpy of association of about 60 kJ/mol [42–44].

We calculated E_{HO}^{I} as well as E_{HO}^{SEN} for the formic and acetic acid dimers with the TZVP basis using both functionals (Table 3). Since the results for different functionals are similar, we discuss only the B3LYP calculations for the sake of clarity.

Within the supermolecular approach, we define the hydrogen-bond energy E_{HO}^{I} for one hydrogen bridge in a carboxylic acid dimer as the energy difference between the total energy of the monomer calculated in the dimeric structure and half the dimer total energy. Note that the relaxation of the monomer is not included, because we are interested in the interaction energy in the strict sense (page 1377 of ref. [28]), which differs from the complex dissociation energy by the relaxation energies of the monomers. This is the quantity which is modeled by the SEN method, because the latter makes use of the molecular orbitals of the dimer structure.

We find a hydrogen-bond energy E_{HO}^{I} of 38 kJ/mol per monomer, while the SEN method yields 46 kJ/mol. In the case of acetic acid, our B3LYP result is 41 kJ/mol per hydrogen bridge from the supermolecular approach, while the SEN method yields 47 kJ/mol, in good agreement with literature values for the dissociation energy [45, 46]. The agreement between the supermolecular method and the SEN value is slightly out of the error bounds we were heading for, but a closer analysis shows that a small energy contribution can be attributed to a change in an intramolecular hydrogen-bond interaction, which in the case of the acetic acid dimer contributes 3.2 kJ/mol according to the SEN analysis, smaller than the 5.0 kJ/mol found in the unrelaxed monomer. The supermolecular result of 41 kJ/mol includes, therefore, an energy gain from the intermolecular contribution of 43 kJ/mol and a loss of 2 kJ/mol because of the weaker intramolecular interaction. Notice that this is not the case for the formic acid dimer, where the intramolecular hydrogen bonds are of essentially the same strength in the dimeric structure and in the unrelaxed monomers.

As an example with an intramolecular hydrogen bond we choose malonic acid, HOOC–CH_2–COOH. We find the global minimum to be the conformation where one COOH group is kept in the usual closed form, while the other COOH opens up through rotation of the OH group to establish a hydrogen bridge to the O = C part of the other carboxylic group (left structure in Fig. 3).

To determine the hydrogen-bond energy E_{HO}^{R} from the supermolecular approach we rotate (and partially relax) the COOH group containing the acceptor oxygen atom. The rotational curve is depicted in Fig. 3 and the results are collected in Table 4. At 90° we find the structure with least hydrogen interaction. The energy difference between the optimized structure at 0° and the 90° structure may be attributed solely to the attractive hydrogen interaction. A local minimum is the 170° structure exhibiting a hydrogen bridge to the OH moiety of the rotated COOH acceptor group for which we can also estimate a hydrogen-bond energy.

Again, we get similar results for both functionals. We find the hydrogen-bond energies E_{HO}^{R} to be 30 kJ/mol for the strong hydrogen bond in the 0° and 9 kJ/mol for the weaker bond in the 170° structure using the TZVP basis. To test the effect of the conformational energy change we rotate the COOH group in acetic acid, which can be understood as a model compound of malonic acid where the COOH donor group is substituted by a hydrogen atom. We find for two similar conformations that the energy difference is about 2 kJ/mol, which should be added to the calculated E_{HO}^{R} since the maximum of the rotational energy curve is less stable than the staggered conformation at 0°. We arrive at 32 kJ/mol for the strong hydrogen bond and at 11 kJ/mol for the weak hydrogen bond. From the SEN method we obtain 31 kJ/mol, in very good agreement with the supermolecular result. At first glance, the strength of the weak hydrogen bond seems to be overestimated by the SEN method, which

Table 3. Results for formic acid and acetic acid dimers calculated with the TZVP basis set. A1 denotes the relaxed monomer, A2 stands for the strained monomer as found in the relaxed dimer structure (B). The energy value for the optimized structure of the relaxed monomer is taken as the reference for the total energetics. E^{I}_{HO}, the energy for a single intermolecular hydrogen bond, is equal to (A2)−1/2 × B. All energies are given in kJ/mol

		E_{DFT}	BP86/RI				E_{DFT}	B3LYP			
			Intramonomer		Intermonomer			Intramonomer		Intermonomer	
			σ_{HO}	E^{SEN}_{HO}	σ_{HO}	E^{SEN}_{HO}		σ_{HO}	E^{SEN}_{HO}	σ_{HO}	E^{SEN}_{HO}
HCOOH											
	A1	0.0	0.0115	4.4	–	–	0.0	0.0102	5.3	–	–
	A2	10	0.0075	2.9	–	–	6	0.0068	3.5	–	–
	1/2 × B	−34	0.0063	2.4	0.1335	51	−33	0.0061	3.1	0.0889	46
	E^{I}_{HO}	45					38				
AcOH											
	A1	0.0	0.0124	4.7	–	–	0.0	0.0111	5.7	–	–
	A2	12	0.0112	4.3	–	–	7	0.0098	5.0	–	–
	1/2 × B	−35	0.0067	2.5	0.1381	53	−34	0.0065	3.3	0.0922	47
	E^{I}_{HO}	47					41				

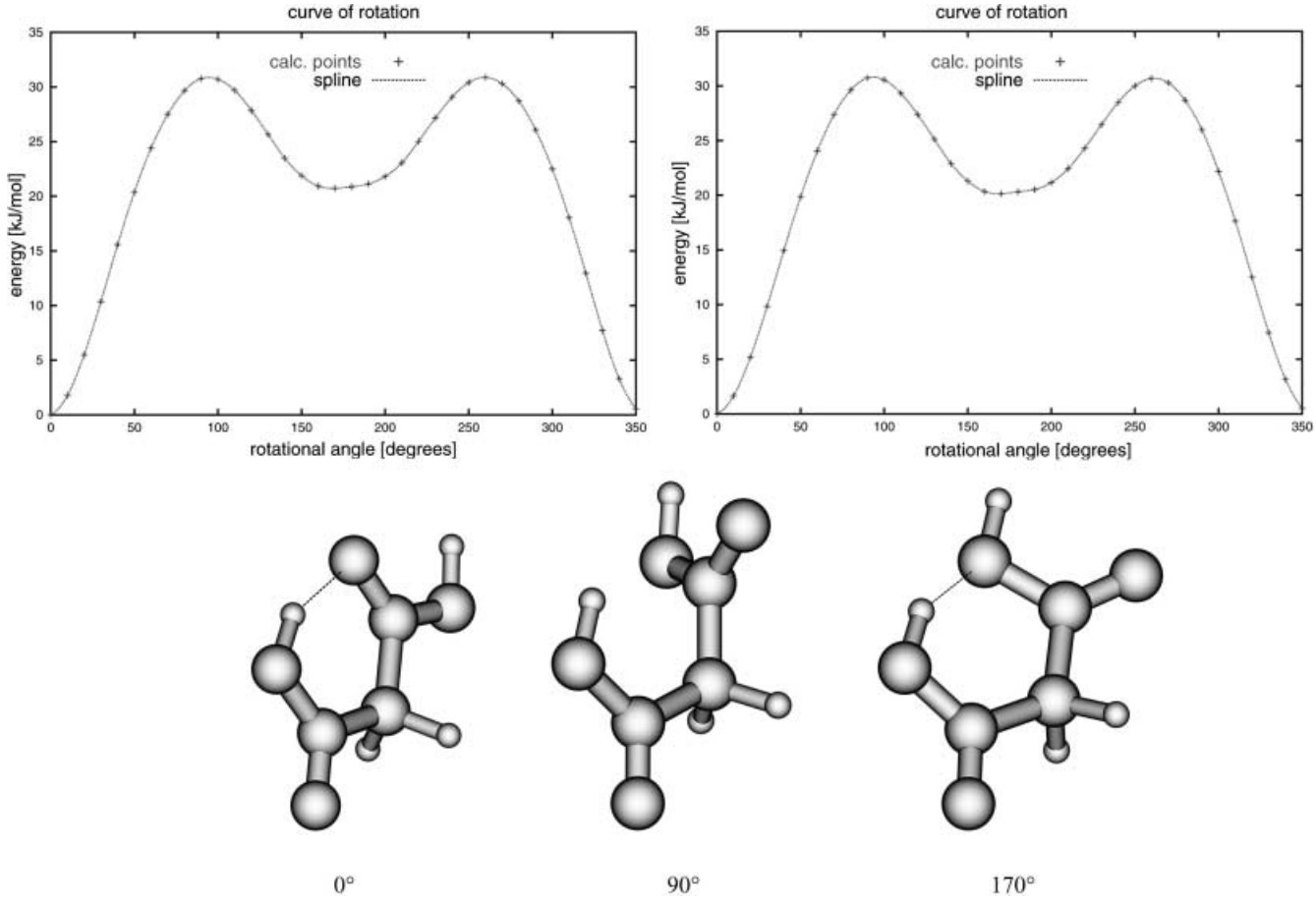


Fig. 3. Curve of rotation of a certain conformation of malonic acid HOOC–CH_2–COOH (BP86/RI l*eft* and B3LYP *right* using the TZVP basis). During the rotation the structure was partially relaxed

yields 22 kJ/mol. We can, however, again improve on this result by closer inspection of the SENs. It turns out that the 90° structure contains a nonnegligible OH···C hydrogen-bond interaction to the C atom of the COOH acceptor group. This interaction is made possible by the large distance to the oxygen atoms of the COOH group, for which the hydrogen-bonding interaction is turned off, and the polarization of the carbon atom by the electronegative oxygens. The increase in energy, i.e., $\Delta E^{SEN}_{HC} = E^{SEN}_{HC,90°} - E^{SEN}_{HC,minimum}$, for this OH···C interac-

Table 4. Results with the TZVP basis set for the three extremum conformations of malonic acid in Fig. 3, i e. at 0°, 90° and 170°. The supermolecular results are given in the E_{HO}^{R} columns. The result line gives the rotation energies as calculated from the shared-electron number results, i.e., $E_{HO}^{R(SEN)} = E_{HO}^{SEN} - \Delta E_{HC}^{SEN}$, where $\Delta E_{HC}^{SEN} = E_{HC}^{SEN}(90°) - E_{HC}^{SEN}(X)$ is the difference in hydrogen-bond energy for the –COO–H···COOH contacts in the zero-energy reference conformation at 90° and a minimum conformation, where X = 0°,170°. All energies are given in kJ/mol

Malonic acid	BP86/RI					B3LYP				
	E_{HO}^{R}	H···O contact		H···C contact		E_{HO}^{R}	H···O contact		H···C contact	
		σ_{HO}	E_{HO}^{SEN}	σ_{HC}	E_{HC}^{SEN}		σ_{HO}	E_{HO}^{SEN}	σ_{HC}	E_{HC}^{SEN}
90°	0.0	–	–	0.0320	12	0.0	–	–	0.0285	15
0°	30	0.0826	31	0.0169	6	30	0.0645	33	0.0130	7
		$E_{HO}^{R(SEN)} = 25$					$E_{HO}^{R(SEN)} = 25$			
170°	9	0.0569	22	0.0050	2	9	0.0490	25	–	–
		$E_{HO}^{R(SEN)} = 11$					$E_{HO}^{R(SEN)} = 11$			

tion has to be subtracted from the E_{HO}^{SEN} energies to get energy values $E_{HO}^{R(SEN)}$, which are conceptually in better agreement with those from the supermolecular approach that always yields energies owing to the change of many interactions. We thus arrive at a value of 25 kJ/mol for the global minimum structure at 0°, while we get 11 kJ/mol for the 170° structure. Taking these additional interactions into account, we obtain very good agreement between E_{HO}^{R} and $E_{HO}^{R(SEN)}$.

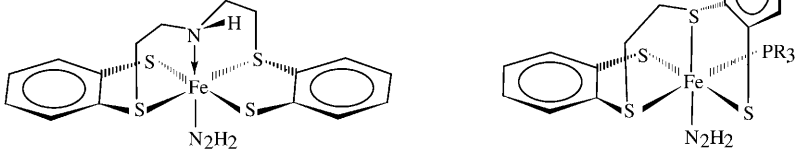
We now turn to our target molecules, the nitrogenase model complexes. We first evaluate the strength of an intramolecular hydrogen bond on the basis of the SEN method. It turns out that for these molecules it is also possible to calibrate the values provided by SENs by means of supermolecular data.

5 Application to transition-metal compounds: diazene-coordinating Fe(II)–S complexes

We investigate two iron–sulfur complexes with diazene (diimide) as a ligand, $[Fe(N_HS_4)(N_2H_2)]$ (**1**) and $[Fe(S_4)PR_3\ (N_2H_2)]$ (**2**) (Fig. 4). These compounds bear structural motifs which qualify them as building blocks of model complexes for the first elementary reduction steps of nitrogenase activity [12]. Here we try to assess the importance of intramolecular hydrogen bridges from the diazene moiety to the sulfur functionalities, since this kind of interaction is expected to stabilize the diazene intermediate in the course of the reduction of a nitrogen molecule to ammonia.

The model compounds which we are going to study are experimentally known only as dinuclear complexes [15, 47]; however, the experimentally unknown mononuclear species which we chose for our study exhibit all the structural features which are also apparent in their dinuclear analogues. Among these diazene complexes, the dinuclear analogue of **1**, $\{\mu\text{-}N_2H_2[Fe(N_HS_4)]_2\}$, is the first example in which diazene binds to low-spin Fe(II) centers carrying only biological compatible donor atoms. It is an important part of the "open-side" FeMoco model [12] that the closed cage structure of the FeMoco opens when nitrogenase moves from the resting into the turnover state.

We chose the two model compounds such that they differ considerably in their coordination spheres and, therefore, are supposed to react in qualitatively different ways. The ligand sphere of **1** consists of one chelate ligand with four in-plane sulfur atoms. Thus, two different sulfur functionalities are involved in the coordination of the Fe(II) center: two thiolate sulfurs and two thioether sulfurs. In contrast with **1**, in compound **2** the four sulfur atoms are in an orthogonal configuration, where one sulfur atom is on top of the plane spanned by the three other sulfur atoms, and the fifth ligand is a phosphane. Again, two sulfur atoms are connected via a bridge such that two thiolate sulfur atoms and two thioether sulfur atoms can be identified in the ligand sphere of the Fe(II) center. The phosphine ligands which yield stable *trans*-diazene compounds in the experiment are, for example, $P(CH_3CH_2CH_2)_3$ and $P(CH_3CH_2CH_2CH_2)_3$ moieties. Stipulating that these ligands can be replaced by $P(CH_3)_3$



$[Fe(N_HS_4)(N_2H_2)]$ N_2H_2-**1**

$[Fe(S_4)PR_3(N_2H_2)]$ N_2H_2-**2**

Fig. 4. Two diazene model compounds, **1** and **2**, which are expected to emulate a key intermediate in the biological nitrogen fixation problem

without crucially changing the electronic structure of the complex, we adopt a slightly simplified model here for the sake of computational efficiency.

The application of the supermolecular approach to these transition-metal compounds requires a detailed description of the optimized structures; this is given in the next section.

5.1 Structural parameters

The optimized structures of the diazene complexes are depicted in Figs. 5 and 6. In the case of compound **1** we find the coordinated *trans*-diazene almost parallel to the axis containing the thiolate sulfurs, whereas the *cis*-diazene is aligned almost parallel to the axis connecting the thioether sulfurs, where the lone-pair repulsion between diazene N and the thioether S is expected to be slightly weaker than the repulsion of diazene N and thiolate S lone pairs.

We find similar alignment of the diazenes in compound **2**, although in **2** the *cis*-diazene is rotated out of the alignment owing to the repulsive interaction with the $P(CH_3)_3$ moiety. The detailed structures are given in terms of Cartesian coordinates as well as selected internal coordinates in the supplementary material.

Among the sulfur–hydrogen distances two are of particular interest since they give structural evidence for the existence of hydrogen bonds: For trans **1** these are about 265 and 245 pm and for trans **2** they are about 253 and 260 pm. We therefore expect to find two hydrogen bonds, which we call long and short, respectively. Qualitatively one would expect that the 245-pm hydrogen bond in **1** will be strong and the 265-pm bond weak. The hydrogen–sulfur distances vary by as much as 5 pm with the density functional and the basis set because the potential well for a hydrogen bond is very shallow.

For the cis **1** structure we do not find hydrogen bonds on the basis of a distance criterion: the shortest sulfur–hydrogen distance is larger than 278 pm. We therefore do not expect to find quantitative evidence for hydrogen bonding in cis **1**. By contrast, cis **2** contains a 258–268-pm hydrogen–sulfur distance (depending strongly on the quantum chemical method used), suggesting the existence of a hydrogen bond.

5.2 Hydrogen-bond energies

Hydrogen bond energies E_{HS}^{SEN} as estimated from the SEN method are shown in Table 5. We attribute only to those hydrogen–sulfur distances a bond energy if the SEN is larger than 0.005. We find that both *trans*-diazene compounds, trans **1** and trans **2**, contain two hydrogen bonds. The energy of the long hydrogen bond is about 8–9 kJ/mol for trans **1** and about 12 kJ/mol for trans **2**. Notice that the dependence of these hydrogen-bond energies on the density functional and on the basis set is surprisingly small. The dependence on the functional is slightly larger for the short hydrogen bond in trans **1**, for which we obtain 15–20 kJ/mol. For the short hydrogen bond in the case of trans **2** we get 8–10 kJ/mol, which is less than the 12 kJ/mol for the corresponding long hydrogen bond. However, the distances between the hydrogen and the sulfur atoms are approximately the same for both hydrogen bridges in complex

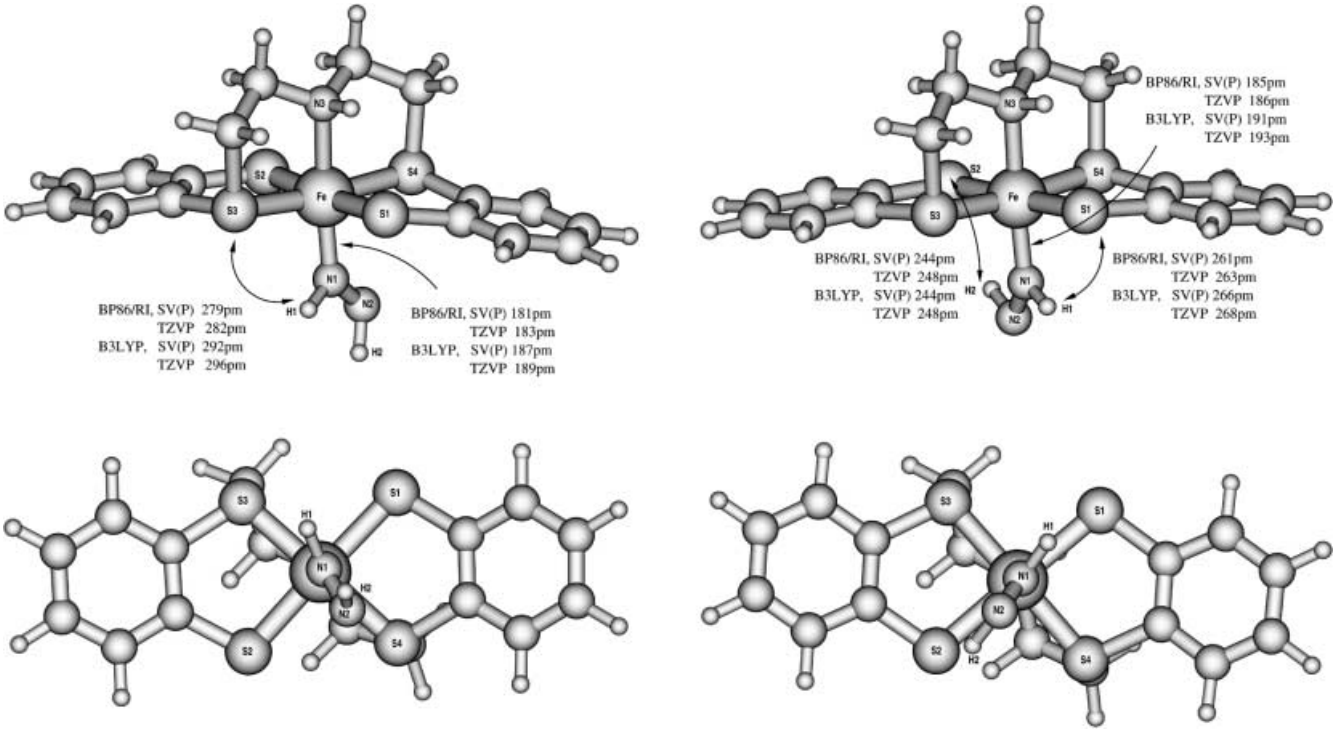


Fig. 5. Side and bottom view of structure of **1** with *cis*-diazene (*left*) and *trans*-diazene (*right*). Short S–H contacts and Fe–N bond distances are given

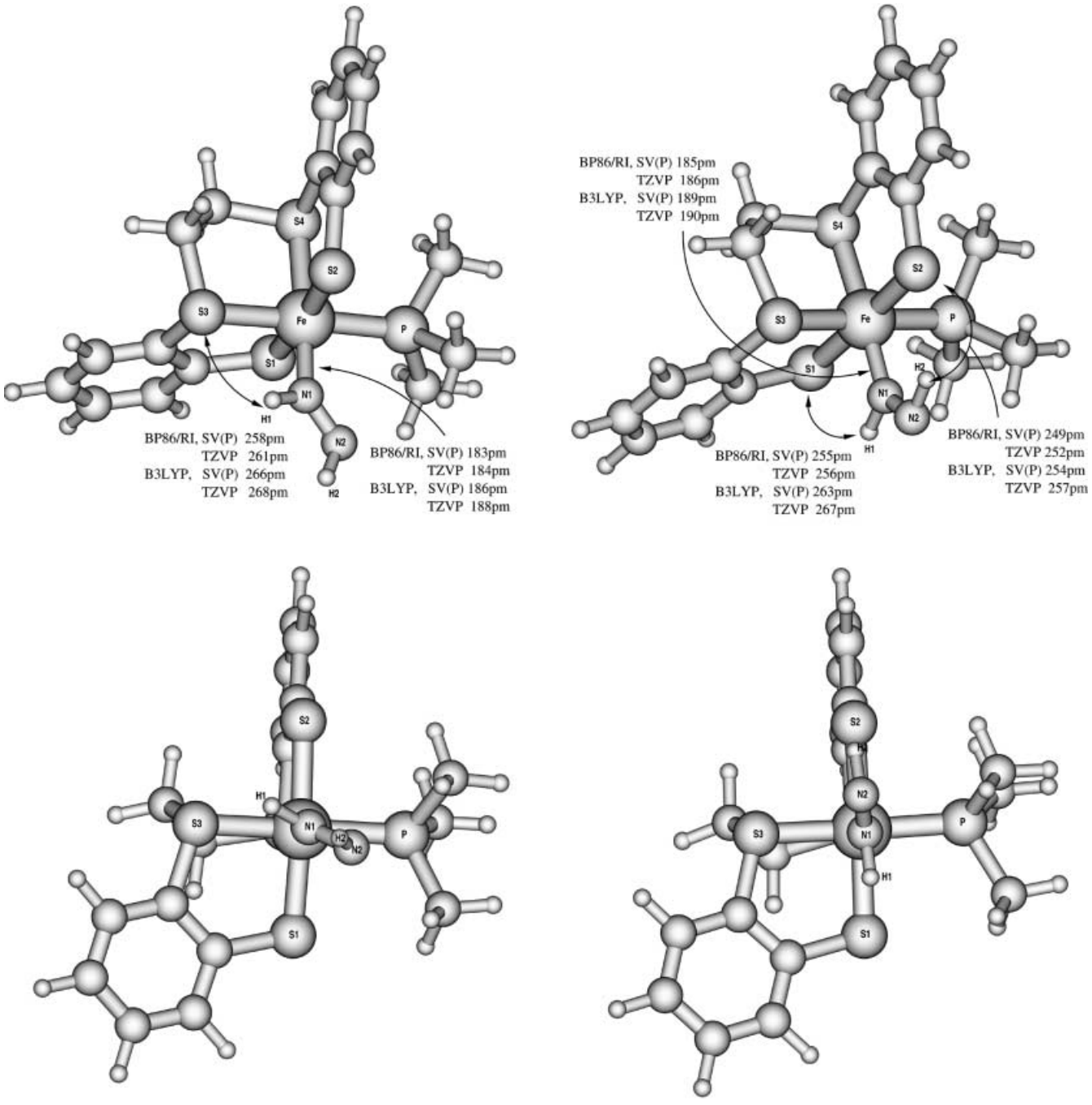


Fig. 6. Side and bottom view of structure of **2** with *cis*-diazene (*left*) and *trans*-diazene (*right*). Short S–H contacts and Fe–N bond distances are given

trans **2** and, therefore, we find almost equal bonding energies, whose small difference cannot be resolved by our method.

For cis **1** we do not find a hydrogen bond. By contrast, cis **2** exhibits a weak one, whose energy is about 5 kJ/mol, as we would have expected in view of its relatively short H···S distance when compared with cis **1**.

Since in **1** and **2** the hydrogen bridges are essentially intramolecular, a calculation of E^{I}_{HS} is not possible. We rather determine an additional descriptor for the strength of the hydrogen bond by considering a rotation of trans-diazene, which breaks the hydrogen bridges which are present in the minimum structure. The corresponding energy curves are given in Figs. 7 and 8.

The rotation of *trans*-diazene in **1** exhibits an almost symmetric rotational energy curve, reflecting the local symmetry of the compound (Fig. 7). Because of the different sulfur functionalities, namely the thiolate and the thioether, we find two minima where the *trans*-diazene is aligned along the thiolate axis and two maxima where it is found along the thioether axis. Since the interaction of the diazene with the sulfur atoms is attractive through-

Table 5. Hydrogen bond energies E_{HS}^{SEN} in kJ/mol for global minima of model compounds **1** and **2** estimated from SENs according to Eq. (3)

Complex	Method							
	BP86/RI				B3LYP			
	SV(P)		TZVP		SV(P)		TZVP	
	σ_{HS}	E_{HS}^{SEN}	σ_{HS}	E_{HS}^{SEN}	σ_{HS}	E_{HS}^{SEN}	σ_{HS}	E_{HS}^{SEN}
trans **1**	0.0359	18	0.0391	15	0.0358	23	0.0385	20
	0.0165	8.2	0.0200	7.6	0.0146	9.3	0.0175	9.0
trans **2**	0.0203	10	0.0203	7.7	0.0158	10	0.0166	8.5
	0.0244	12	0.0303	12	0.0189	12	0.0204	11
cis **2**	0.0110	5.5	0.0118	4.5	0.0084	5.4	0.0092	4.7

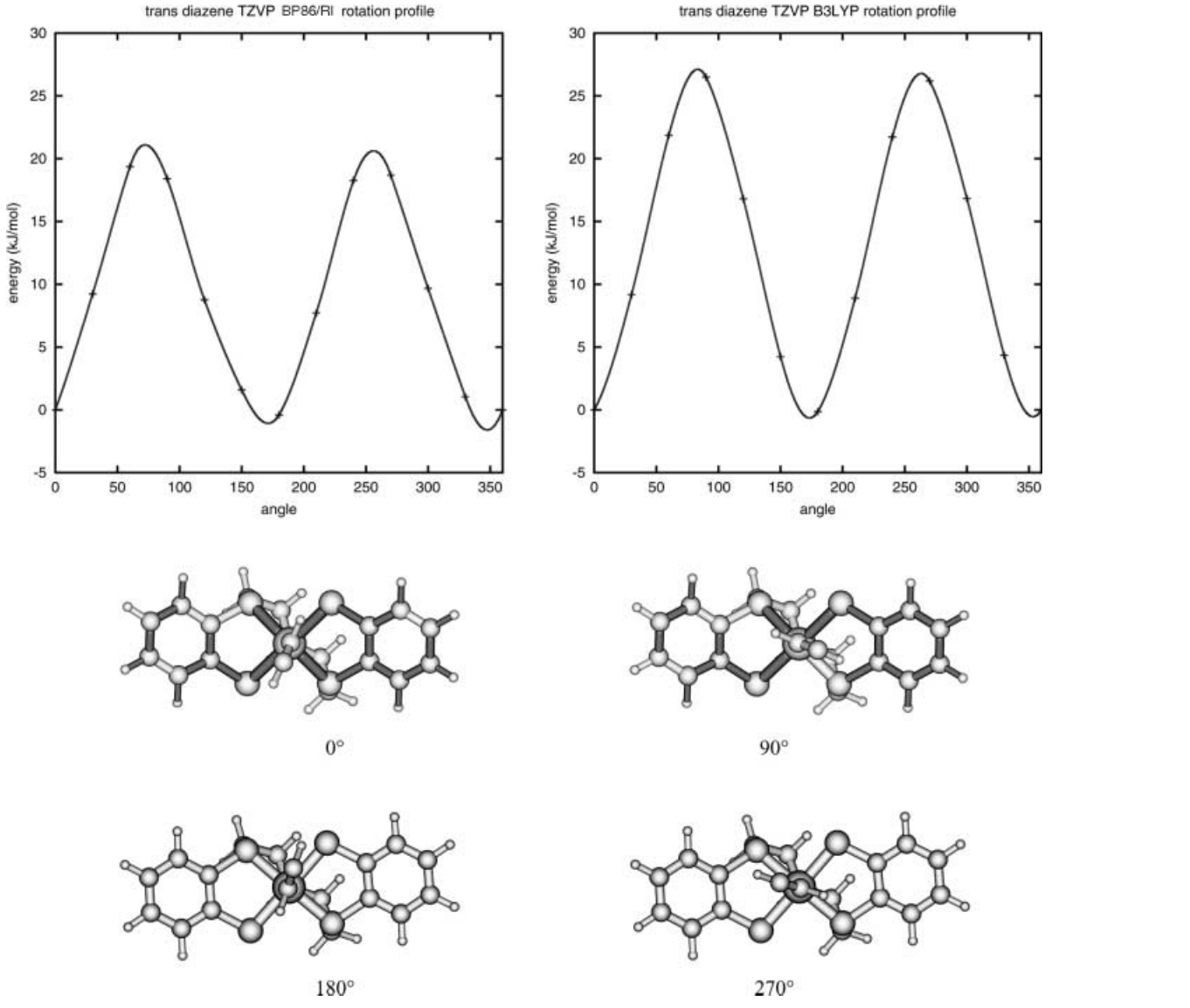


Fig. 7. Curve of rotation of *trans*-diazene coordinated in **1** (BP86/RI *left* and B3LYP *right* using the TZVP basis). The zero point of rotational energy is fixed arbitrarily. Note that the hydrogen atoms are not aligned with the S–Fe–S axes since they always point into the direction of the lone pairs of the sulfur

out, we take the difference of the maxima and minima of the rotation curve as a lower bound for the energy of the two hydrogen bridges present at the minimum structure. We do not find SENs larger than 0.005 in the 90° rotamer, where it is parallel to the thioether sulfurs, so we conclude that the residual attraction is below 5 kJ/mol.

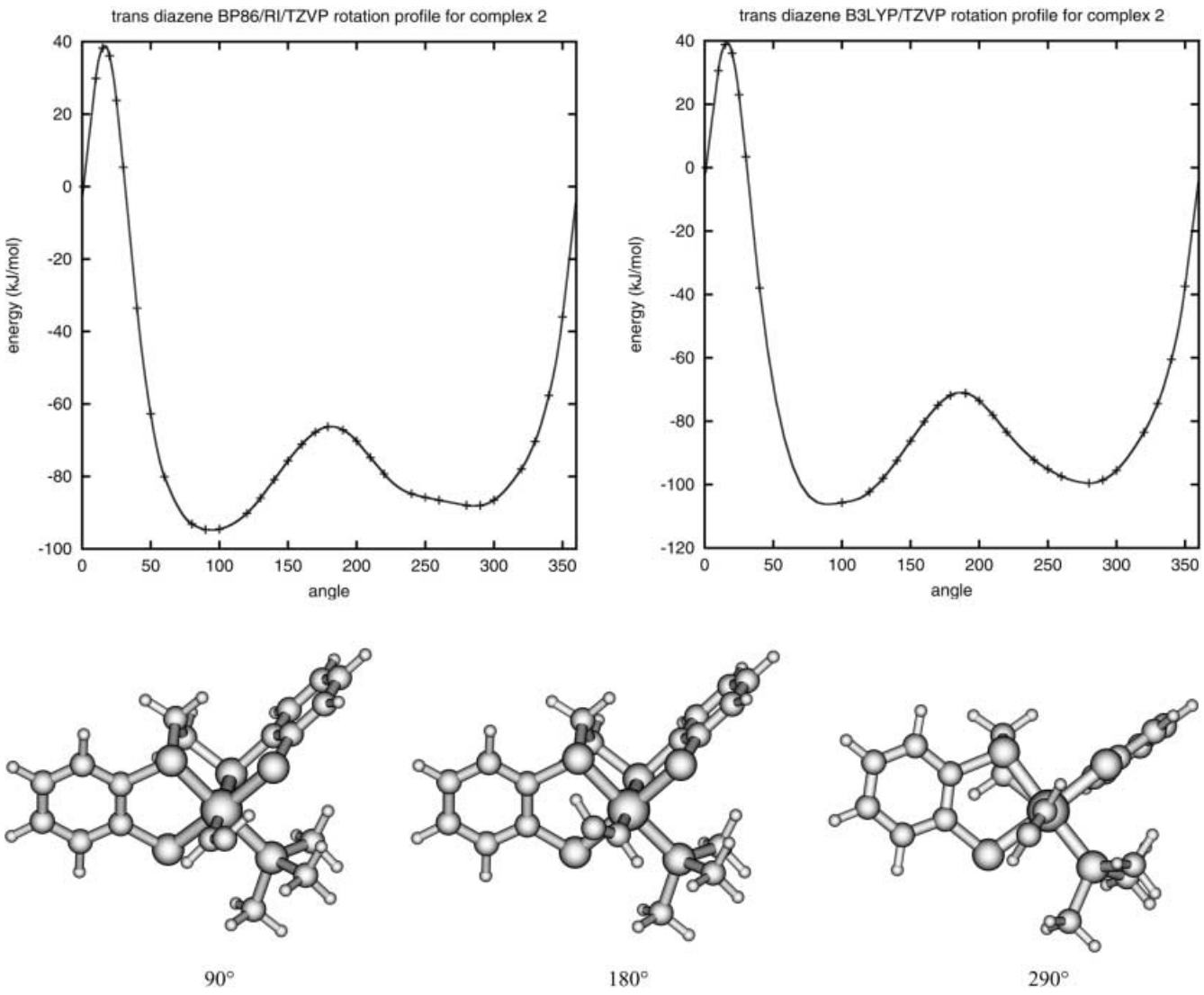


Fig. 8. Curve of rotation of *trans*-diazene coordinated in **2** (BP86/RI *left* and B3LYP *right* using the TZVP basis set). The structural parameters given in Sect. 5.1 correspond to the global minimum at 90°. The zero point of rotational energy is fixed arbitrarily

Indeed, we find a value for E_{HS}^{R} of 26 kJ/mol in the case of the B3LYP functional and 20 kJ/mol for the BP86/RI functional, in very good agreement with the corresponding E_{HS}^{SEN} values of 29 and 23 kJ/mol, respectively.

The rotational energy curve of *trans*-diazene in **2** shows two minima (at 90° and 270°), where the diazene molecule is oriented along the thiolate axis (Fig. 8). Moreover, two maxima exist, at 20° and 180°. The global maximum at 20° is not helpful for our purpose since it is due to a H–H repulsion of the diazene H atom and the $P(CH_3)_3$ group which is kept fixed during rotation.

Both minimum structures feature two hydrogen bonds, while only one is possible for the 180° structure, where one diazene hydrogen atom points to the $P(CH_3)_3$ group; however, in the 180° structure a possible hydrogen bond would also be of different quality since the hydrogen atom is close to a *thioether* sulfur atom. Assuming that the attractive energy contribution by the thioether bridge is negligible compared to the repulsive interaction of the other diazene hydrogen atom with the $P(CH_3)_3$ group, we can give an upper bound for the hydrogen-bond energies at the minimum structures of less than 30 kJ/mol for BP86/RI and less than 40 kJ/mol for B3LYP.

5.3 cis-Diazene versus trans-diazene coordination

We might try to estimate the hydrogen-bond energy E_{HS}^{iso} from the difference in the total energy of the cis and trans compounds. In this approach we would have to assume that both isomers coordinate to the iron center in essentially the same way, which is indeed not the case because we find that *cis*-diazene is more strongly bound in both model complexes than *trans*-diazene. This is obvious from the Fe–N bond distances: for **1** we find an about 4 pm shorter Fe–N distance for the cis isomer compared with the trans form, while this distance is 2–3 pm shorter in cis **2** than in trans **2**.

Table 6. Relative energies ΔE_{iso} in kJ/mol of the *trans*- and *cis*-diazene isomers in the gas phase ΔE_{iso}^{gas} and as the global minimum of the rotational energy curve ΔE_{iso}^{coor}. E_{HS}^{iso} denotes the difference in the stabilization energy of both diazene isomers. For comparison, the G2 result for the isomerization energy is 22.3 kJ/mol [60]

Complex		BP86/RI		B3LYP	
		SV(P)	TZVP	SV(P)	TZVP
	ΔE_{iso}^{gas}	25.5	26.3	27.1	27.9
1	ΔE_{iso}^{coor}	29.4	30.8	38.3	38.2
	E_{HS}^{iso}	3.9	4.5	11.2	10.3
2	ΔE_{iso}^{coor}	23.0	25.0	29.9	31.3
	E_{HS}^{iso}	−2.5	−1.3	2.8	3.4

The results for isomerization energies for *trans*- and *cis*-diazene in their minimum structures in the gas phase and coordinated to **1** and **2**, respectively, are given in Table 6. The gas-phase isomerization energies of the free ligands are about 28 kJ/mol and almost independent of the density functional and the basis set. For the complexes the difference in the energies obtained from different functionals is comparatively large and amounts to 8 kJ/mol.

Focusing on the B3LYP/TZVP results, we find that the N_2H_2 isomerization energies are increased by 10 kJ/mol in **1** and do not change appreciably in the case of **2** compared to the uncoordinated diazene isomers. The 10 kJ/mol difference in **1** is due to two effects: firstly, *trans*-diazene forms hydrogen bonds, which tend to increase the isomerization energy by $E_{HS}^{SEN} = 30$ kJ/mol; secondly, *cis*-diazene does not form hydrogen bonds, but is bound more strongly to the [Fe(N_HS_4)] fragment. To yield consistent energetics for the coordination process of the diazene isomers, we can attribute 20 kJ/mol to this additional stabilization of *cis*-diazene.

The different stabilization effects when the diazene isomers bind to complex fragments **1** and **2** are shown in Fig. 9. The 20 kJ/mol increase in the coordination energy of *cis*-diazene compared to *trans*-diazene is also consistent with an essentially unchanged isomerization energy for **2**: here, we take into account a contribution of $E_{HS}^{SEN} = 20$ kJ/mol for the hydrogen bonds in the *trans*-diazene complex, which is therefore stabilized by the same amount of energy as *cis*-diazene, yielding in total the unchanged isomerization energy. The energetics of this process are compared to those of **1** in Fig. 9.

Since an analysis of the rotation curve of the cis isomer does not reveal a substantial effect of a π-type bond of diazene to the metal center, we attribute the increased bond strength of the cis isomer predominantly to the interaction of the permanent dipole moment of *cis*-diazene with the dipole moment of the complex, giving an increased electrostatic attraction compared to the trans isomer.

6 Conclusion

Making use of various descriptors, we were able to attribute values for the energy contributions of hydrogen bridges in diazene complexes **1** and **2**. Since supermolecular descriptors were found to be of limited use because they typically include a variety of different interactions, we found that the most versatile descriptor is provided by a new method which determines an energy value for a hydrogen bridge by means of the SEN between the hydrogen atom and the acceptor atom. We established a linear relationship between the SEN and the hydrogen-bond energy by means of a fit to a set of simple hydrogen-bonded molecular complexes and validated the method by applying it to hydrogen bonds in formic and acetic acid dimers and malonic acid.

The motivation for our study was the attempt to determine quantitatively the energetic stabilization which is provided by the formation of hydrogen bridges in diazene complexes modeling potential nitrogenase intermediates. We studied two model complexes and employed two independent approaches, namely the SEN method and the interpretation of the rotational curve of diazene.

We determined values based on SENs for the two hydrogen bridges in trans **1** and trans **2**. Depending on the functional, we obtained for trans **1** 8–9 kJ/mol for the long and 15–20 kJ/mol for the short hydrogen bond (thus, about 25–30 kJ/mol for both bridges). For trans **2** we got 8–9 kJ/mol for the short and 11–12 kJ/mol for the long hydrogen bond (i.e., about 20 kJ/mol for both bridges). By an independent supermolecular method, namely a rotation curve of *trans*-diazene in **1**, we obtained a lower bound of 20–26 kJ/mol, in very good agreement with the SEN result. Other supermolecular approaches, which study isomerization processes or the decomposition of the complex into molecular fragments, are not applicable for the complexes under study. Note that these supermolecular approaches always involve more quantum chemical calculations than needed for the SEN approach.

For the two model compounds we found that both trans complexes possess two relatively strong hydrogen–sulfur bonds. They are of different strength in **1**, but of similar strength in **2**. The hydrogen-bond strength can be modulated through the hydrogen–sulfur distance, which itself is determined through the ligand sphere, provided that the hydrogen atom points in the direction of a sulfur lone pair. In particular, for H–S distances which are larger than 270 pm we do not find hydrogen bonding in **1** and **2** according to the SEN criterion that σ_{HA} must be larger than 0.005.

Our examples have demonstrated the usefulness of the SEN method: The method provides an easily accessible criterion for the existence of a hydrogen bond within a complex structure and permits the assignment of an energy value to the hydrogen bond which describes a contribution to the stabilization of the entire structure. The method is easy to apply, sufficiently reliable for chemical purposes and sufficiently general to warrant further studies in different context. It permits separation of various effects brought about in the electronic structure on formation of the hydrogen bridge, which are lumped into a single number in the supermolecular approach. In particular in intramolecular hydrogen bridges, this single number is not even measurable, and analysis has to resort to a method based on local

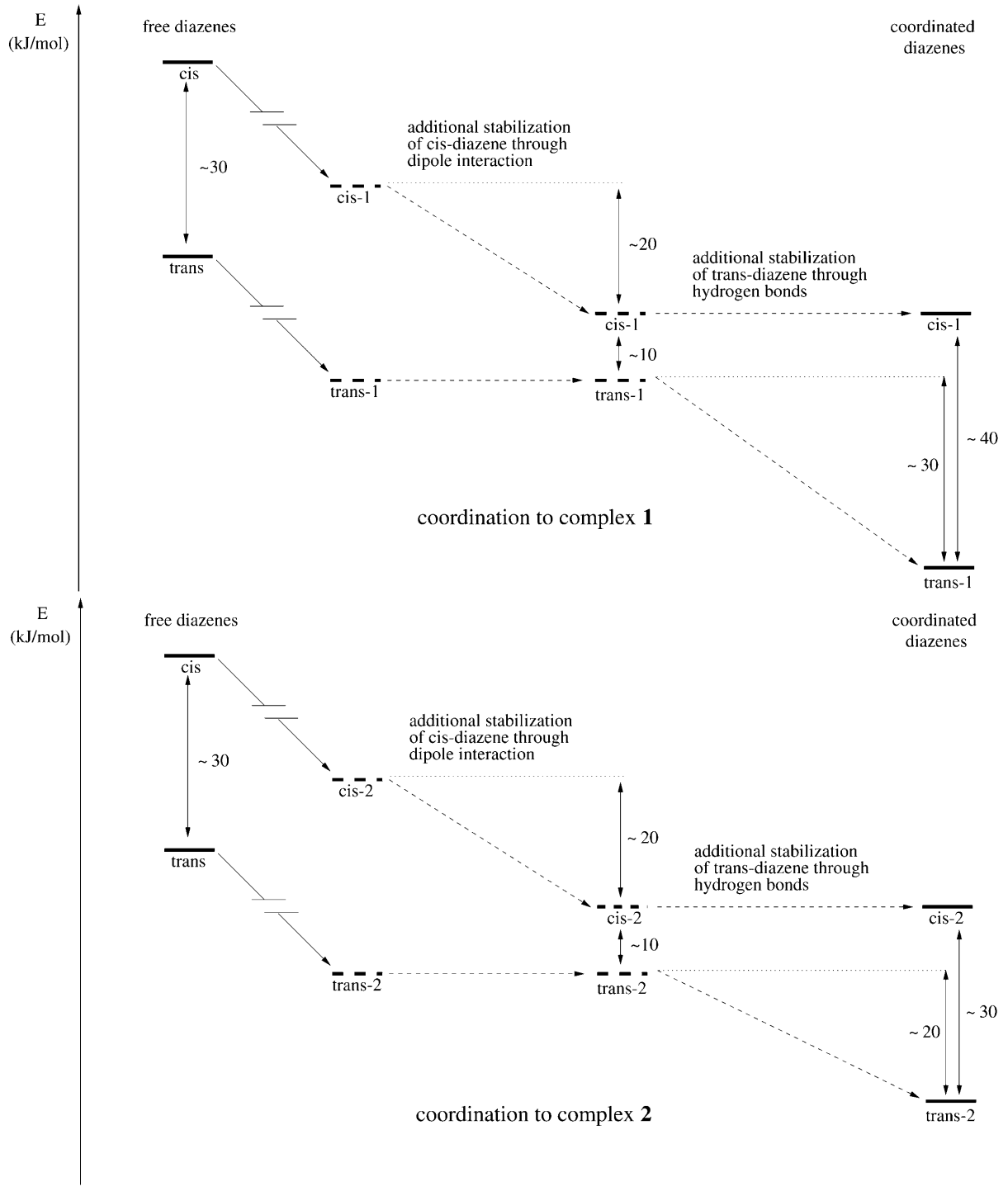


Fig. 9. Relative energetics of the coordination process of *cis*-diazeneand *trans*-diazene to complex fragments **1** and **2** starting with the uncoordinated isomers (*left*). We shifted the center of energy owing to coordination by the pure *trans*-diazene–Fe binding energy in step one. The next step shows the additional stabilization of *cis*-diazene by about 20 kJ/mol followed by tan increase in stabilization energy of the trans isomer owing to hydrogen-bond interaction, yielding, on the *right-hand side*, the final situation in **1** (*top*) and **2** (*bottom*)

properties of the wavefunction rather than total energy calculations. The SEN method offers a way to accomplish this. The error margin of 5–10 kJ/mol is acceptable, bearing in mind that the supermolecular calculations, whenever applicable, are also of limited accuracy. Errors of this size can often be tolerated when discussing the properties of structural motifs with practical applications in mind. The calculations discussed have further shown that results obtained with the BP86/RI method are accurate enough for the determination of E_{HA}^{SEN}, although the B3LYP energetics is generally considered to be more reliable [48]. Since BP86/RI calculations are computationally much more efficient, it is gratifying that the accuracy of the method does not

deteriorate seriously when choosing the more efficient method. It appears to us that one should probably not go below TZVP basis-set quality, since values obtained with the smaller SV(P) basis set have considerably larger errors, of the order of 10–15 kJ/mol in the cases we investigated.

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Appendix: quantum chemical methodology

For all the calculations we used the density functional programs provided by the Turbomole 5.1 suite [49]. We employed the Becke–Perdew functional dubbed BP86 [50, 51] and the hybrid functional B3LYP [52, 53] as implemented in Turbomole. Moreover, for the BP86 functional we always used the resolution of the identity (RI) technique [54, 55]. All the results were obtained from all-electron restricted Kohn–Sham calculations. The assumption of a singlet ground state for the Fe(II)–S compounds is justified since unrestricted test calculations for the lowest lying triplet and quintet states have shown that these are always higher in energy.

The influence of the size of the basis set was studied by means of two different basis sets, the first denoted SV(P). This is the Ahlrichs split-valence basis set [56] with polarization functions on heavy atoms, but not on hydrogen atoms. Moreover, the TZVP basis featuring a valence triple-zeta basis set with polarization functions on all the atoms was used [57]. All the structures were optimized with the corresponding basis set, unless otherwise stated. For the calculation of rotational barriers of the diazene complexes, we report only TZVP results, since the energetics of the conformers turned out to be fairly independent of the basis set. In order to analyze the electron density of the compounds, we made use of the concept of SENs as implemented in Turbomole.

The program MOLDEN [58] was used for the visualization of the structures.