Behavior of interactions between hydrogen chalcogenides and an anthracene π-system elucidated by QTAIM dual functional analysis with QC calculations†‡

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The nature of EH₂⋅−⋅−π(C₁₄H₁₀) interactions (E = O, S, Se and Te) of an anthracene system was elucidated by applying QTAIM dual functional analysis (QTAIM-DFA) after clarification of the structural features with quantum chemical (QC) calculations. π-HB (hydrogen bond) interactions were detected for E = O, S, Se and Te, whereas π-EB (chalcogen bond) interactions were observed for E = O in (EH₂)⋅−⋅−π(C₁₄H₁₀), where the bond paths connected H in EH₂ to C₁₄H₁₀ in π-HB, and they connected E in EH₂ to C₁₀H₈ in π-EB. The QTAIM-DFA parameters of (R, θ) and (θp, κp) were evaluated for the interactions via analysing the plots of H(p) versus H(q) and V(q) versus H(r)/2 for the interactions at the bond critical points. Data obtained from the perturbed structures around the fully optimized structures were employed for the plots, in addition to the fully optimized structures. Data obtained from the fully optimized structures were analysed using (R, θ), which corresponded to the static nature, and those obtained from the perturbed structures were analysed using (θp, κp), which represented the dynamic nature of the interactions, where θp corresponds to the tangent line of the plot and κp is the curvature. The θ and θp values are less than 90° for all the interactions examined, except for the H⋅−⋅−11C(π) interaction in TeH₂⋅−⋅−π(C₁₄H₁₀) (C₁: IIIB₉), where H is located closer to the centre of C₁₀H₈. Therefore, the interactions examined were predicted to have vdW nature, appeared in the pure-CS (closed shell) interaction region, although H⋅−⋅−11C(π) was predicted to have the pure-CS/typical-HB nature without covalency. Additionally, the π-HB interaction seems to be slightly stronger than π-EB in (OH₂)⋅−⋅−π(C₁₄H₁₀).

Introduction

Significant attention has been paid to the interactions between hydrogen chalcogenides (EH₂: E = O, S, Se and Te) and aromatic π-systems, and some structures have been reported for benzene adducts formed through π-interactions.¹⁻⁸ The interactions in benzene π-systems are mainly characterized by the hydrogen bonds formed between EH₂ and the benzene π-system, which act as a proton donor and proton acceptor, respectively, and have been called hydrogen bonds of the π-type (π-HBs) herein.¹⁻⁸ The π-HB (hydrogen bond) interactions were also investigated for 1 : 1 and 2 : 1 adducts between EH₂ (E = O and S) and the naphthalene π-system.⁹⁻²⁰ Indeed, there have been many investigations on π-adducts, which are mainly based on a theoretical background; however, these investigations seem to be rather limited to structural features. The nature of the π-HB interactions has seldom been reported, especially for the anthracene π-system, π(C₁₄H₁₀), to the best of our knowledge.

Very recently, we reported the nature of the EH₂⋅−⋅−π interactions for benzene and naphthalene π-systems, together with their structural features.¹⁻³,¹⁸,¹¹ The H atom(s) in EH₂ is (are) connected to the benzene π-system, EH₂⋅−⋅−π(C₆H₆), via bond paths (BPs). Through careful examination of the BPs in the adducts, another type of interaction was also detected in H₂E⋅−⋅−π(C₆H₆), where E in EH₂ is joined to the benzene π-system via a BP. Such interaction was called a chalcogen π-type (π-EB) bond. EH₂ is connected to the C atoms or BCPs (bond critical points: r_C-C on the C=C bonds of C₆H₆) by BPs. In the case of the benzene π-system, π-EBs seem more important relative to π-HBs, although the predicted importance may change depending on the calculation system.²

What happens if EH₂ (E = O, S, Se and Te) interacts with the anthracene π-system? The anthracene π-system contains two types of (three) benzene π-systems and one type of (two)
naphthalene $\pi$-system, in addition to the original anthracene $\pi$-system. What are the differences and similarities in the EH$_2$$\cdots$$\pi$ interactions between the anthracene $\pi$-system and the $\pi$-systems of naphthalene and benzene? The nature of the interactions in (EH$_2$)$\cdots$$\pi$([C$_4$H$_{10}$]) ($E = O, S, Se$ and Te) is elucidated together with its structural feature. Scheme 1 illustrates some of the structures expected for (EH$_2$)$\cdots$$\pi$([C$_4$H$_{10}$]) of the 1 : 1 adducts, which are inferred from the structures of (EH$_2$)$\cdots$$\pi$([C$_{10}$H$_8$]) and (EH$_2$)$\cdots$$\pi$([C$_6$H$_6$]), respectively. Interactions between the anthracene, electron energy densities are plotted around the central and outer benzene rings of anthracene, respectively, whereas it is above the 11C-14C (or 13C-14C) bond in type IA$_{Atc}$. The structures for the 1 : 1 adduct of (EH$_2$)$\cdots$$\pi$([C$_4$H$_{10}$]) are defined for the adduct, where EH$_2$ locates on the central benzene rings of anthracene, respectively, whereas it is above the 11C-14C (or 13C-14C) bond in type IA$_{Atc}$. The structures for the 1 : 1 adduct of (EH$_2$)$\cdots$$\pi$([C$_4$H$_{10}$]) are also shown in Scheme 1 for convenience of discussion. The optimized structures are called type IA$_{Bzn}$, IB$_{Bzn}$ and type IIA$_{Bzn}$ for (EH$_2$)$\cdots$$\pi$([C$_6$H$_6$]) and type I$_n$ap and type II$_n$ap for (EH$_2$)$\cdots$$\pi$([C$_{10}$H$_8$]).

The QTAIM (quantum theory of atoms-in-molecules) approach, introduced by Bader,$^{22,23}$ enables the analysis of the nature of chemical bonds and interactions.$^{24-30}$ Interactions seem to be defined by the corresponding BPs, but we must be careful to use the correct terminology with the concept.$^{31}$ BCP is an important concept in QTAIM, which is a point along the BP at the interatomic surface, where charge density, $\rho(r)$, reaches a minimum.$^{22,23}$ It is denoted by $\rho_0(r_0)$, in addition to other QTAIM functions at BCPs, such as Laplacians of $\rho(r)$ ($\nabla^2 \rho_0(r_0)$), total electron energy densities $H_0(r_0)$, potential energy densities $V_0(r_0)$ and kinetic energy densities $G_0(r_0)$, together with $k_0(r_0) = V_0(r_0)/G_0(r_0)$.

Recently, we proposed QTAIM dual functional analysis (QTAIM-DFA)$^{33-36}$ according to QTAIM.$^{22-30,37}$ QTAIM-DFA enables experimental chemists to analyse their own results concerning chemical bonds and interactions with their own image.$^{38}$ QTAIM-DFA provides an excellent possibility for evaluating, classifying and understanding weak to strong interactions in a unified form.$^{35-36}$ To elucidate the nature of the interactions in question with QTAIM-DFA, $H_0(r_0)$ is plotted versus $H_0(r) - V_0(r)/2 = (h^2/8m)^2 \rho_0(r_0)$, where both the $x$ and $y$ axes are given units of energy. In our treatment, data for perturbed structures around fully optimized structures are employed for the plots, in addition to the fully optimized structures.$^{33-36}$ We propose the concept of “the dynamic nature of interactions” which originated from the data containing the perturbed structures.$^{38,40,47}$

Data from the fully optimized structures correspond to the static nature of interactions. QTAIM-DFA is applied to typical chemical bonds and interactions and rough criteria are established. The rough criteria can distinguish the chemical bonds and interactions in question from others. QTAIM-DFA and the criteria are explained in the ESI with Schemes S1 and S2, Fig. S1 and eqn (S1)-(S7). The basic concept of the QTAIM approach is also surveyed.

QTAIM-DFA is applied to elucidate the dynamic and static nature of the interactions in (EH$_2$)$\cdots$$\pi$([C$_{14}$H$_{10}$]) ($E = O, S, Se$ and Te). The discussion is limited to the 1 : 1 adducts of (EH$_2$)$\cdots$$\pi$([C$_{14}$H$_{10}$]) for simplicity. Herein, we present the results of the investigations on the nature of the interactions in question. The interactions are classified and characterized as a reference by employing the criteria.

### Methodological details in calculations

Structures were optimized using the Gaussian 09 programs.$^{48}$ The 6-311+G(3df) basis set$^{49}$ was employed for O, S and Se and the basis set of the (743111/743111/7411/2 + 1s1p1d1f) type from Sapporo Basis Set Factory$^{50}$ was used for Te with the 6-311+G(d,p) basis set$^{45}$ for C and H. The basis set system (BSS) is called BSS-F according to examinations of the BSSs in a previous study. The Möller–Plesset second order energy correlation (MP2) level$^{43}$ was applied to the calculations. Optimized structures were confirmed by the frequency analysis.

QTAIM functions were calculated by employing the wfn files using the Gaussian 09 program package$^{48}$ with the same method for optimizations, and the data were analysed with the AIM2000 program.$^{44}$ The normal coordinates of internal vibrations (NIV) obtained by the frequency analysis were employed to generate the perturbed structures.$^{35,36}$ which is explained in eqn (1). The $k$-th perturbed structure in question ($S_{kw}$) was generated by the addition of the normal coordinates of the $k$-th internal vibration ($N_k$) to the standard orientation of a fully optimized structure ($S_0$) in the matrix representation.$^{35}$ The coefficient $f_{kw}$ in eqn (1) controls the difference in the structures between $S_{kw}$ and $S_0$. $f_{kw}$ is determined to satisfy eqn (2) for the interaction in question, where, $r$ and $r_0$ stand for the distances in question in the perturbed and fully optimized structures, respectively, with $a_0$ of Bohr radius (0.52918 Å). The perturbed structures with NIV correspond to that with $r$ being elongated or shortened by 0.05$a_0$ or 0.1$a_0$, relative to $r_0$, as shown in eqn (2). $N_k$ of five digits are used to predict $S_{kw}$. The selected vibration must contain the motion of the interaction in question most effectively among all the zero-point internal vibrations.

$$S_{kw} = S_0 + f_{kw}N_k$$  \hspace{1cm} (1)

$$r = r_0 + w_{kw} (w = (0), \pm 0.05 \text{ and } \pm 0.1; a_0 = 0.52918 \text{ Å})$$  \hspace{1cm} (2)
\[ y = c_0 + c_1x + c_2x^2 + c_3x^3 \] 

\((R^2:\text{square of correlation coefficient}).\)

In the QTAIM-DFA treatment, \(H_0(r_c)\) is plotted versus \(H_0(r_c) - V_b(r_c)/2\) for data of five points of \(w = 0, \pm 0.05\) and \(\pm 0.1\), as shown in eqn (2). Each plot is analysed using a regression curve of the cubic function, as shown in eqn (3), where \((x, y) = (H_0(r_c) - V_b(r_c)/2, H_0(r_c))\) \((R^2 \geq 0.999999\) usually).  

Results and discussion

Structural feature of \((\text{EH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\) (\(\text{E} = \text{O, S, Se and Te}\))

Before the final structural optimizations for \((\text{EH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\) (\(\text{E} = \text{O, S, Se and Te}\)), the minima were searched for systematically with MP2/BSS-F. The search was started assuming typically type \(\text{IA}_{\text{Atc}}\) type \(\text{IB}_{\text{Atc}}\) and type \(\text{IC}_{\text{Atc}}\) structures of the \(\text{C}_1\) symmetry. The type \(\text{IA}_{\text{Atc}}\) and type \(\text{IB}_{\text{Atc}}\) structures of \((\text{EH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\) were optimized for \(\text{E} = \text{O and S}\), whereas only type \(\text{IB}_{\text{Atc}}\) was optimized for \(\text{E} = \text{Se and Te}\). The processes of the convergence are summarized in Table S1 of the ESI.†

The type \(\text{IA}_{\text{Atc}}\) structure optimized for \((\text{OH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\) with MP2/BSS-F was apparently different from type \(\text{IB}_{\text{Atc}}\), as confirmed by the \(r_1\) values. In the case of \((\text{SH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\), one structure was optimized, which was close to the type \(\text{IA}_{\text{Atc}}\) structure if initially assuming a typical type \(\text{IA}_{\text{Atc}}\) structure. The type \(\text{IA}_{\text{Atc}}\) structure optimized for \((\text{SH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\) \((\text{SH}_2\cdot\cdot\pi(\text{C}_{14}\text{H}_{10})\): \(\text{IA}_{\text{Atc}}\)) seems somewhat distorted from the \(\text{C}_1\) symmetry. The search converged to another one, if started assuming typical type \(\text{IB}_{\text{Atc}}\) and type \(\text{IC}_{\text{Atc}}\) structures, which are close to type \(\text{IA}_{\text{Atc}}\). Indeed, their \(r_1\) values are very close to each other, but the \(\phi_1\) and \(\phi_2\) values seem meaningfully different for the two types (Fig. 1c and d, respectively). Therefore, the second structure is (tentatively) called type \(\text{IB}_{\text{Atc}}\), herein. No type \(\text{IA}_{\text{Atc}}\) structures were detected after similar treatment, even if optimizations started from those very close to type \(\text{IA}_{\text{Atc}}\).

Table 1 collects the structural parameters selected for the optimized structures of \((\text{EH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\) (\(\text{E} = \text{O, S, Se and Te}\)), \(r_1, r_2, r_3, \theta_1, \theta_2, \phi_1, \phi_2\) and \(\phi_3\), which are defined in Scheme 2. The optimized structures are not shown in the figures, but they can be found in molecular graphs, which are drawn on the optimized structures (see Fig. 1). What factors appear to control the optimized structures? We compared the \(\text{H}··\text{H}\) distance in \(\text{EH}_2\), \(r(\text{H}, \text{H}: \text{EH}_2)\), with the \(11\text{C}··13\text{C}\) distance in \(\text{C}_{14}\text{H}_{10}\), \(\text{r}(11\text{C}, 13\text{C}: \text{C}_{14}\text{H}_{10})\). Indeed, \(r(\text{H}, \text{H}: \text{EH}_2)\) for \(\text{E} = \text{O (1.522 Å), S (1.931 Å), Se (2.088 Å) and Te (2.361 Å)}\) is shorter than \(r(11\text{C}, 13\text{C}: \text{C}_{14}\text{H}_{10})\) \((2.452 Å for \text{central benzene ring})\), but the differences in \(r(\text{H}, \text{H}: \text{EH}_2)\) for \(\text{E} = \text{O (1.522 Å), S (1.931 Å), Se (2.088 Å) and Te (2.361 Å)}\) are larger than 0.5 Å for \(\text{O (1.930 Å)}\) and \(\text{S (0.5215 Å)}\), whereas they are smaller than 0.4 Å for \(\text{Se (0.3644 Å) and Te (0.0913 Å)}\) (see Table S2 of the ESI†). The type \(\text{IB}_{\text{Atc}}\) structures of \((\text{EH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\) \((\text{E} = \text{O, S, Se and Te})\) would form with no limitations of \(\Delta r\), whereas it may be necessary for \(\Delta r\) larger than around 0.5 Å to give the type \(\text{IA}_{\text{Atc}}\) structures \((\text{E} = \text{O and S}).\) In the case of type \(\text{IB}_{\text{Atc}}\), one \(\text{H}\) in \(\text{EH}_2\) seems to be slightly above the \(11\text{C}··13\text{C}\) bond for \(\text{E} = \text{Se and Te},\) but \(\text{OH}_2\) seems to exist almost right above the \(11\text{C}··13\text{C}\) bond, which may also be controlled by \(\Delta r\). Indeed, the difference in \(\Delta r\) between \(\text{E} = \text{S and Se}\) seems small, at a first glance, but the small difference would play an important role in the appearance of the type \(\text{IA}_{\text{Atc}}\) structure.

What are the stabilization energies in the formation of the adducts? Table 1 contains the \(\Delta E (\Delta E_{\text{ES}}\) and \(\Delta E_{\text{Ent}}\)) values for \((\text{EH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})\), where, \(\Delta E_{\text{ES}}\) and \(\Delta E_{\text{Ent}}\) are the \(\Delta E\) values on the energy surfaces and those with the thermal corrections to enthalpies, respectively \([\Delta E = \Delta E((\text{EH}_2)\)··\(\pi(\text{C}_{14}\text{H}_{10})) - \Delta E(\text{EH}_2) + E(\text{C}_{14}\text{H}_{10}))\)]. An excellent correlation was obtained in the plot of \(\Delta E_{\text{Ent}}\) versus \(\Delta E_{\text{ES}}\) \((y = 5.262 + 1.047x; R^2 = 0.998 (n = 6; number of data points)),\) although is not shown in the figure. Therefore,
Table 1 Structural parameters for (EH2)...π(C14H10) (E = O, S, Se and Te) optimized at the MP2 level with BSS-F

| Species (X-Y) (symmetry: type) | r1 (Å) | r2 (Å) | r3 (Å) | θ1 (°) | θ2 (°) | θ3 (°) | ϕ1 (°) | ϕ2 (°) | ϕ3 (°) | ∆EES (kJ mol⁻¹) | ∆EEnt (kJ mol⁻¹) |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|----------------|-----------------|
| OH⋯π(C14H10) (C1; IIaAc)      | 3.2865 | 0.9629 | 0.9629 | 89.9   | 51.8   | 103.5  | −92.5  | −1.7   | 2.8    | −22.7          | −18.1           |
| H2O⋯π(C14H10) (C1; IIbAc)     | 3.6682 | 0.9631 | 0.9624 | 63.4   | 69.6   | 103.6  | −93.8  | −14.3  | 3.5    | −21.9          | −17.6           |
| SH⋯π(C14H10) (C1; IIaAc)      | 3.6162 | 1.3389 | 1.3400 | 80.5   | 60.6   | 92.2   | −92.1  | −6.4   | −3.3  | −28.7          | −25.0           |
| SH⋯π(C14H10) (C1; IIbAc)      | 3.6165 | 1.3389 | 1.3400 | 80.5   | 60.6   | 92.2   | −91.8  | −2.1   | −1.9  | −28.7          | −25.0           |
| SeH⋯π(C14H10) (C1; IIaAc)     | 3.6959 | 1.4597 | 1.4603 | 78.9   | 61.5   | 91.3   | −91.5  | 3.0    | −0.2  | −31.7          | −28.3           |
| TeH⋯π(C14H10) (C1; IIaAc)     | 3.7703 | 1.6576 | 1.6578 | 78.1   | 64.2   | 91.5   | −89.9  | −11.4  | −17.5 | −40.5          | −36.8           |

*a* BSS-F: the 6-311+G(3df) basis set was employed for O, S and Te and the basis set of the (743111/743111/74111/2 + 1s1p1d1f) type for Te with the 6-311++G(d,p) basis set for C and H.

**Molecular graphs and contour plots of ρ(r) for (EH2)⋯π(C14H10)**

Fig. 1 illustrates the molecular graphs for (EH2)⋯π(C14H10) (E = O, S, Se and Te), which were calculated with MP2/BSS-F. The BCPs are clearly detected, which contain that expected between EH2 and C14H10. Each BP with BCP joins O in OH2 and a carbon atom in 11Co r 13Ci nC 14H10 for all optimized structures of Table 2, except for the type IIbAc of H2O⋯π(C14H10). The BP with BCP joins O in OH2 and a carbon atom in 11Co r 13Ci nC 14H10 for all optimized structures of Table 2, except for the type IIbAc of H2O⋯π(C14H10), the interaction of which should be classified by the π-EB type. Ring critical points (RCPs) and cage critical points (CCPs) are also detected in Fig. 1. Fig. 2 also shows the contour plots of ρ(r) for (EH2)⋯π(C14H10) (E = O, S, Se and Te) calculated with MP2/BSS-F. The contour plots of ρ(r) are drawn on a plane containing E, BCP (r) of the (EH2)⋯π(C14H10) type and an atom or BCP suitable for the contour plots of (EH2)⋯π(C14H10). The BCPs well located at the (dimensional) saddle points of ρ(r) in the species. Negative Laplacians and trajectory plots are drawn in Fig. S2 and S3 of the ESI.† It is well visualized how the BCPs are classified through ∇ρ(r) and the space around the species is well divided by the atoms in it.

**Survey of the interactions in (EH2)⋯π(C14H10) (E = O, S, Se and Te)**

As shown in Fig. 1 and 2, some BPs are apparently curved. Therefore, the lengths of the BPs (rBP) will be substantially different from the straight-line distances (RSL) in some cases. The rBP and RSL values are collected in Table S2 of the ESI.† for (EH2)⋯π(C14H10) (E = O, S, Se and Te), which were evaluated with MP2/BSS-F, together with the differences between rBP and RSL, (ΔrBP = rBP − RSL). There are two types of BPs in each adduct since each adduct has C1 symmetry. Therefore, it is necessary to define the BPs to distinguish the two. Letting H and H1 in EH2 connect to π(C14H10) through BPs, which are placed more inside and more outside, respectively, in relation to the centre of C14H10, then ³BP and ⁴BP can be defined as ³BP (³H⋯π) and ⁴BP (⁴H⋯π), respectively.
Table 2  QTAIM functions and QTAIM-DFA parameters for the interactions in (EH₂)⁺⁻π(C₁₄H₁₀) (E = O, S, Se and Te) evaluated with MP2/BSS-F²

| Interaction               | Type  | ρₐ(rₐ) (e⁻⁻³) | cV²ρ₀(r₀) (au) | H₂O(rₐ) (au) | kₜ(rₜ) | R (au) | θ (°) | ϵₚ (e⁻au⁻³) | Classification characterization |
|---------------------------|-------|----------------|----------------|--------------|----------|--------|-------|------------|----------------------------------|
| OH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIAAc | IIABC | 0.0060 | 0.0024 | 0.0007 | −0.814 | 0.0025 | 72.6 | 108.7 | 0.0411 | 74.5 | 8.0 | p-CS/vdW |
| O₂⁻⁻π(C₁₄H₁₀) (C₁): type IIAAc | IIABC | 0.0069 | 0.0029 | 0.0009 | −0.831 | 0.0031 | 73.9 | 104.5 | 0.0346 | 79.3 | 18.1 | p-CS/vdW |
| SH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc | IIABC | 0.0065 | 0.0024 | 0.0007 | −0.835 | 0.0025 | 74.2 | 65.9 | 0.0151 | 74.3 | 145.7 | p-CS/vdW |
| SeH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc | IIABC | 0.0070 | 0.0027 | 0.0009 | −0.799 | 0.0025 | 71.5 | 65.8 | 0.0161 | 73.6 | 37.3 | p-CS/vdW |
| Se₂⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc | IIABC | 0.0065 | 0.0024 | 0.0007 | −0.836 | 0.0025 | 74.2 | 65.8 | 0.0161 | 73.4 | 61.8 | p-CS/vdW |
| Se₂⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc | IIABC | 0.0072 | 0.0028 | 0.0100 | −0.789 | 0.0029 | 70.8 | 54.6 | 0.0158 | 72.7 | 30.4 | p-CS/vdW |
| TeH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc | IIABC | 0.0070 | 0.0025 | 0.0008 | −0.829 | 0.0029 | 73.7 | 50.3 | 0.0086 | 93.8 | i | p-CS/HBac |
| Te₂⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc | IIABC | 0.0088 | 0.0031 | 0.0008 | −0.849 | 0.0032 | 75.3 | 23.9 | 0.0082 | 82.9 | 299.8 | p-CS/vdW |

² BSS-F: the 6-311+G(3df) basis set employed for O, S and Se and the basis set of the (7433111/743111/7411/2 + 1s1p1d1f) type for Te with the 6-1GA basis set. Other details as in Table 1.

Fig. 2  Contour plots of ρ(r) for OH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIAAc (a), H₂O⁻⁻π(C₁₄H₁₀) (C₁): type IIAAc (b), SH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc (c), SH₂⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc (d), SeH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc (e) and TeH₂+⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc (f), calculated with MP2/BSS-F. The BCPs on the plane are denoted by red dots, those outside of the plane are denoted as black dots. RCPs by blue squares, CCPs by green dots and bond paths on the plane by black line and those outside of the plane by grey lines. Carbon atoms are in black and hydrogen atoms are in grey, with the other atoms in black. The contours (ea⁻³) are at Z = ±8. ±7, ..., 0 with 0.0047 (heavy line).

The Δρₐp values are small (ca. 0.03 Å) for ¹BP (Se₂⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc). Thus, the Δρₐp values can be approximated as straight lines. However, the Δρₐp value is large (0.41 Å) for ¹BP (Se₂⁻⁻π(C₁₄H₁₀) (C₁): type IIBAc), which seems difficult to be approximated by a straight line. The values remain moderate (0.09–0.17 Å) for most of the π-HB and π-EB interactions in EH₂⁺⁻π(C₁₄H₁₀) for E = O, S, Se and Te, other than three cases. The BCPs could be approximated as almost straight lines to gentle curves. The rₛ values are plotted versus Rₛ in Fig. 3. A very good correlation was obtained for the case of 0.09 ≤ Δρₐp ≤ 0.17 Å, which is shown in the figure. The data for three BPs deviate from the correlation, although two of them can be approximated as straight lines, as mentioned above.

The QTAIM-DFA was applied to the interactions between EH₂ and C₁₄H₁₀ in EH₂⁺⁻π(C₁₄H₁₀) (E = O, S, Se and Te) and the QTAIM functions were calculated for the interactions at BCP. The results are given in Table 2. Fig. 4 shows the plot of H₂(rₐ) versus H₂(rₐ) for EH₂⁺⁻π(C₁₄H₁₀) (E = O, S, Se and Te), which contains the data for the perturbed structures evaluated with MP2/BSS-F. All the data in Fig. 4 appear in the area of H₂(rₐ) > 0.0, which belongs to the pure-CS (closed shell: p-CS) region. The plots were analysed according
The criteria tell us that $45^\circ < \theta < 90^\circ$ for pure-CS interactions. The $\theta_p$ value predicts the character of the interactions. In the p-CS region, the character of the interactions will be the vdW type for $45^\circ < \theta_p < 90^\circ$, whereas it will be the $t$-HB (typical hydrogen bonds) type with no covalency ($t$-HB$_{nc}$) for $90^\circ < \theta_p \leq 125^\circ$, where $\theta_p = 125^\circ$ tentatively corresponds to $\theta = 90^\circ$.

The $\theta$ and $\theta_p$ values are less than 90° for all the $\pi$-HBs and $\pi$-EB in EH$_2$-$\pi$(C$_{14}$H$_{10}$) examined herein, except for the Te$^+$H$^+$H$^+$-$\pi$(C$_{14}$H$_{10}$) interaction in TeH$_2$-$\pi$(C$_{14}$H$_{10}$). Therefore, the $\pi$-HBs and $\pi$-EB interactions in EH$_2$-$\pi$(C$_{14}$H$_{10}$) in Table 2 are all classified by the pure-CS interactions and characterized as the vdW type (p-CS/vdW), except for Te$^+$H$^+$H$^+$-$\pi$(C$_{14}$H$_{10}$). Although $\theta^\circ$BP (Te$^+$H$^+$H$^+$-$\pi$(C$_{14}$H$_{10}$)) is predicted to have the nature of (p-CS/vdW), $\delta^\circ$BP (Te$^+$H$^+$H$^+$-$\pi$(C$_{14}$H$_{10}$)) is predicted to have the nature of (p-CS/$t$-HB$_{nc}$). The $\pi$-EB interaction in the H$_2$O-$\pi$.1.C(C$_{14}$H$_{10}$) type [$[\theta_\pi, \theta_p] = (73.9^\circ, 79.3^\circ)$] is predicted to be somewhat stronger than the $\pi$-HB interaction of the O$-$H$\cdots$C($\pi$) type [$[\theta_\pi, \theta_p] = (72.6^\circ, 74.5^\circ)$] for OH$_2$-$\pi$(C$_{14}$H$_{10}$).

The $\pi$-HB interactions in the anthracene system are predicted to be very similar to that in the naphthalene system, which seem slightly stronger than that in the benzene system. The results are in accordance with that derived from the energies for the formation of the adducts.

The delocalization indexes and ellipticity are the important parameters to clarify and understand the nature of the (EH$_2$)-$\pi$ interactions. The nature of the (EH$_2$)-$\pi$ interactions will be discussed elsewhere based on these parameters for the series of (EH$_2$)$\cdots$-HB(C$_n$H$_{2n}$), (EH$_2$)$\cdots$-EB(C$_n$H$_{2n}$), and (EH$_2$)$\cdots$-EB(C$_{14}$H$_{10}$) (E = O, S, Se and Te).

**Conclusions**

The behaviour of the interactions for EH$_2$ adducts with the anthracene $\pi$-system (E = O, S, Se and Te) in a 1 : 1 ratio is elucidated by applying QTAIM-DFA. The structures were optimized with MP2/BSS-F. Two types of structures were optimized for E = O and S, whereas one was optimized for E = Se and Te. The BCPs are clearly detected in the molecular graphs. The interactions are the $\pi$-HB type for EH$_2$-$\pi$(C$_{14}$H$_{10}$) (C$_1$: IIA$_{Ac}$) (E = O and S) and EH$_2$-$\pi$(C$_{14}$H$_{10}$) (C$_1$: IIB$_{Ac}$) (E = S, Se and Te), whereas they are the $\pi$-EB type for H$_2$O-$\pi$(C$_{14}$H$_{10}$) (C$_1$: IIB$_{Ac}$). The QTAIM-DFA parameters of ($R$, $\theta$) and ($\theta_p$, $\kappa_p$) are calculated for the species, according to eqn (S3)–(S6). The $\theta$ values are less than 90° for all interactions examined in this work. The $\theta_p$ values are also less than 90° for all the interactions in question, except for $^{1}H$-$\pi$.1.C($\pi$) in TeH$_2$-$\pi$(C$_{14}$H$_{10}$) (C$_1$: IIB$_{Ac}$). Therefore, all the $\pi$-HB and $\pi$-EB interactions examined in this work are classified by pure-CS interactions and characterized as vdW in nature (p-CS/vdW), although $^{1}H$-$\pi$.1.C($\pi$) in TeH$_2$-$\pi$(C$_{14}$H$_{10}$) (C$_1$: IIB$_{Ac}$) is predicted to have the p-CS/$t$-HB nature without covalency. The $\pi$-EB interaction is predicted to be somewhat stronger than $\pi$-HB in (OH$_2$)-$\pi$(C$_{14}$H$_{10}$). It is demonstrated that the predicted nature of EH$_2$-$\pi$(C$_{14}$H$_{10}$) is closer to that of EH$_2$-$\pi$(C$_{10}$H$_8$) rather than that of EH$_2$-$\pi$(C$_{5}$H$_8$). The $\pi$-HB and $\pi$-EB interactions in the anthracene $\pi$-system are well elucidated by applying QTAIM-DFA.
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$\pi(C_4H_{10})$ are clearly detected by BPs with BCPs which is another reason to use BPs and BCPs in this work.

32 Critical points (CPs) are characterized by the rank ($\omega$) and the signature ($\sigma$). The CPs of the species in the three-dimensional space are classified by $\omega = 3$, which generally corresponds to all species. On the other hand, $\sigma$ is defined by the simple algebraic sum of the signs of $\partial^2 \rho(r_i)/\partial r_i^2$ ($r_i = x, y$ and $z$ for $i = 1, 2$ and 3, respectively), where the + and - signs of $\partial^2 \rho(r_i)/\partial r_i^2$ are counted as +1 and -1, respectively. Therefore, $\sigma = -3, -1, 1$ and 3 correspond to attractors (nuclei), bond critical points (BCPs), ring critical points (RCPs) and cage critical points (CCPs), respectively. Namely, BCP is characterized by $(\omega, \sigma) = (3, -1)$.

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39 The concept of a dynamic molecular graph was recently proposed by Corte’s-Guzmania and co-workers through the investigation of the Born–Oppenheimer molecular dynamics (BOMD), which was exemplified by [Fe(C-(CH$_3$)$_3$)$_2$(CO)$_3$]$_3$. The investigation illustrates the change in the behaviour of the molecular graph. The concept of the dynamic molecular graph would be closely related to that of the dynamic nature of interactions predicted by employing the perturbed structures generated with the normal coordinate of internal vibrations (NIV). In this treatment, the selected vibration for NIV must contain the motion of the interaction in question most effectively among all the zero-point internal vibrations. A structural catastrophe is confirmed not to occur for the perturbed and fully optimized structures for the elucidation of the dynamic nature of the interaction in question with NIV.

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