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Density functional studies on trialkyl phosphorus selenide dibromide complexes R_3PSeBr_2 ($R = H$, Me, Et, $N(CH_3)_2$, $N(C_2H_5)_2$, Ph, and C_6H_{11})

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Abstract

R_3PSeBr_2 complexes where R is H, Me, Et, $N(CH_3)_2$, $N(C_2H_5)_2$, Ph, or C_6H_{11} and their parent compounds of the formula R_3PSe have been studied in the gas phase at the density functional theory. Different stationary points on the molecular potential energy surface were located and characterized for each dihalide complex; two energy minima and many saddle points. The minima correspond to the molecular T-shaped (trigonal bipyramidal) and the molecular tetravalent angular geometry at the selenium centre where the dihalide in linear spoke structure. One of the saddle points corresponds to another isomer of the T-shaped structure where the $BrSeBr$ species is almost eclipsed with two of the RP moieties. Solvent effects were modelled using self consistent reaction field Onsager model in the presence of cyclohexane and dichloromethane. Optimized geometries whether in the gas phase or in solution exhibit variation of the $SeBr$ bond distances within the same T-shaped complex. The $P–Se$ double bond character in the parent R_3PSe compounds is no longer retained in the dibrominated ones, in addition, $P–Se$ bond distances in the R_3PSeBr_2 complexes are found R-dependent. All energy calculations are found favouring the T-shaped adducts over the spoke ones. Onsager SCRF calculations reflected significant changes in the geometrical parameters in the R_3PSeBr_2 complexes in solvent with relatively high dielectric constant (dichloromethane) from that provided in the gas phase.
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1. Introduction

The nature of compounds formed as a consequence of reacting tertiary phosphine selenoides with dihalides has received only limited attention where Zingaro et al. were considered as the pioneers in this area of study [1–5]. They reported that the interaction of R_3PSe with dihalogen and interhalogen appeared to form a stable charged transfer 1:1 adduct of the formula R_3PSeXX, where in case of interhalogen complexes, the heavier halogen binds directly to the selenium atom. Similar results have been obtained with the sulfide counterpart in case of dihalogen and interhalogen except with I_2 where an unusual 2:3 adduct of the formula $R_3PSI_2–I_2–I_2SPR_3$ was isolated [6]. In fact these coworkers reported that the 1:1 adduct R_3PSII could be identified in solution but isolated as the 2:3 one in the solid state. This behaviour has been attributed to the poor donor ability of R_3PS toward the diiodine and thus a 2:3 adduct formed of two R_3PSII moieties and a bridging diiodine molecule. This result motivated other workers to re-investigate the reaction of R_3PS with I_2. Kaur and Lobana pointed out that R_3PS formed a 2:3 adduct in the presence of CCl_4 and a 1:1 complex in CH_2Cl_2, concluding, the formation of the 1:1 complex is solvent dependent [7,8]. Ultimately, the existence of the 1:1 R_3PSII complex in the solid state has been decisively confirmed after the isolation of the

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1:1 complex crystals by Bricklebank et al. [9]. Godfrey et al. found out that the reaction of R_3PSe with I_2 ($R = Ph$, Me_2N, Et_2N, or C_6H_{11}) gives the 1:1 adduct both in solution and in solid state [10]. They also found that, on conducting the same reaction with Br_2, a T-shaped geometrical structure around the *Se* centre is obtained which is in contrast to that of the analogous R_3PSeI_2 reported [11]. While the reaction of R_3PS with X_2 ($X_2 = I_2$ or *IBr*) led to the formation of a 1:1 CT complex of the formula R_3PSX_2, the same reaction with Br_2 proved to be more complex. For example, in the case of R_3PS, phosphorous–sulfur bond cleavage occurred and the compound R_3PBr_2 and elemental sulfur are produced [12]. Recently, Godfrey and his co-workers managed to isolate $Ph_4Se_4Br_4$ where four *PhSeBr* units are linked together by weak *Se–Se* bonds forming essentially Se_4 planar ring. The *SeBr* bonds lie in the Se_4 plane with two *Ph* rings lying above the plane, and two below [13].

On the other hand, the four coordinate molecular Ph_3P–*Br–Br* spoke structure was isolated, identified [14] and theoretically studied by us in a previous work [15] where strong $P \ldots Br$ interaction ($\bar{v} = 239\ \mathrm{cm}^{-1}$) is reported. Me_3AsBr–*Br* was reported as well [16].

In this study, the influence of changing *R* group on the geometry of the R_3PSeBr_2 will be investigated, and the existence of another geometry where the *BrBr* moiety adopt a charged transfer spoke structure in addition to the experimentally confirmed T-shaped geometry will be explored.

2. Calculation

A variety of R_3PSeBr_2 where the alkyl substituents are hydrogen (*H*) methyl (*Me*), ethyl (*Et*), *N*,*N*-dimethylamine (Me_2N), *N*-*N*-diethylamine (Et_2N), cyclohexyl (C_6H_{11}),and phenyl (*Ph*) groups, and their R_3PSe parent compounds have been theoretically investigated using the hybrid Density Functional Theory. Molecular geometries were fully optimized in each case in the gas phase using the internal coordinates or the Cartesian coordinates when the internal ones not applicable at the B3LYP/6-311G(d,p) level of theory. The stationary nature of each of the fully optimized structures was examined by harmonic vibrational frequency calculations. Single point B3LYP/6-311+G(3d,2p) calculations were conducted at the stationary point geometries in order to investigate possible deficiencies in the basis set. Solvent effect were modelled using the self consistent reaction field Onsager model [17] with frequency calculations at the same level of theory in the presence of cyclohexane and dichloromethane in case of the T-shaped geometries and in diethylether solution in case of the proposed charged transfer spoke structures. Linear and nonlinear optical properties of these compounds were also numerically calculated using the finite field method [18] in the presence of a step-size 0.001 *au* of electric field along the Cartesian axis with B3LYP/6-311++G(d,p) level of theory. Geometries were constructed in such a way that the *Se*, *Br*, *Br*, and *P* atoms are assigned numbers 1, 2, 3, 4, respectively. Charges are calculated using the standard Mulliken [19] population analysis. The Gaussian 03 series [20] of programs employed for the *ab initio* calculations were run on the University of Manchester high performance computer (Horace) system.

3. Gas phase optimization of R_3PSeBr_2 complexes

Optimization showed that all of the R_3PSeBr_2 investigated compounds are ground states on the potential energy surface. These complexes adopt two different geometries, T-shaped and angular molecular geometries around the selenium centre, approximately, trigonal bipyramidal, and bent angular structures on taking account of the active lone pairs on the selenium atom according to the Valence Shell Electron Pair Repulsion Model (VSEPR). Whereas the T-shaped structure around the *Se* centre is in complete accordance with the single X-ray diffraction studies conducted on $(Me_2N)_3PSeBr_2$ by Godfrey and his co-workers [11], they are in complete contrast with the reported linear spoke crystallographic structure of the iodine counterpart $(Me_2N)_3PSeI$–*I* [10] and $(Me_2N)_3PSI$–*I* by the same co-workers [12]. The other explored bent geometries are in complete accordance with the reported iodine linear spoke structures [12]. Fig. 1 displays selected T-shaped and spoke structures for some of the R_3PSeBr_2 complexes. Hydrogen atoms are omitted for clarity.

4. Energy

We record various energies of all ground state structures in the gas phase in Table 1, in atomic units $E_\mathrm{h} = 4.3598 \times 10^{-18}$ J, which is equal 627.5095 kcal mol^{-1}. All molecular energies included zero-point energies are referred to the fully optimized geometries at the B3LYP/6-311G(d,p) level of theory, and all geometries are true stationary points on the molecular PES. Differences of energies between the T-shaped and spoke structures ΔE calculated using the values in the second and third columns are reported as well.

Apparently, the T-shaped geometries are more stable than the spoke structures in the gas phase at this level of theory. It worth pointing out that the energy of each of the two forms is found lower than the energy sum of the constituent molecules R_3PSe and Br_2.

Complexation energies of each of the T-shaped geometries ΔE_T and of the spoke structures ΔE_S of the dibrominated adducts were calculated as the difference between the total energies of the R_3PSeBr_2 complexes and the sum of the total energies of the isolated R_3PSe adducts and Br_2 molecules in the gas phase under normal conditions of temperature (298.15 K) and pressure (1.0 atm).

In order to investigate the basis set size, we performed single point calculations at the B3LYP/6-311+G(3d,2p) level of theory, using the B3LYP/6-311G(d,p) fully optimized geometries. The results are reported in Table 1 as

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