Ylide Character and Stability of Heterocyclic Benzenes

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ABSTRACT: Optimizations are carried out on heterocyclic benzenes including oxabenzene (1_O), thiabenzene (1_S), selenabenzene (1_{Se}), tellurabenzene (1_{Te}), 1,1-dihydropyridinium (2_N), 1,1-dihydrophosphinium (2_P), 1,1-dihydroarsinium (2_{As}), and 1,1-dihydrostybinium (2_{Sb}), using HF and DFT methods with 6-311++G* basis sets. These partly aromatic compounds have 6π-electrons showing ylide character. Nonplanar boat conformers appear as global minima for 1_X. In contrast, planar conformers are the most stable in 2_X series. The inversion barrier energy of heteroatom in 1_O appears the least in 1_X structures. Ylide character increases in series 1_X and 2_X with the orders of $1_{Te} > 1_O > 1_{Se} > 1_S$ and $2_{As} > 2_N > 2_{Sb} > 2_P$, respectively. Homodesmic studies show stability order for series 1_X to be $1_S > 1_{Se} > 1_{Te} > 1_O$, whereas the order of stability for series 2_X is $2_{As} > 2_P > 2_{Sb} > 2_N$. © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:412–417, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20443

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INTRODUCTION

Ylides may form via connecting a carbon atom carrying an unshared pair of electrons with phosphorus [1], nitrogen [2], sulfur [3], arsenic [4], or selenium [5]. Phosphorus ylides, discovered by Staudinger and Meyer in 1919 [6], are used in the Wittig reactions [7]. Various investigations are performed on interesting structure and reactivity of phosphorus ylides [8]. This more thorough study of the phosphorus ylide is primarily due to its greater stability in solution, its greater ease of preparation, and its greater synthetic utility (the Wittig reagent) compared to the same characteristics of trimethylammonium methylide [9]. Although phosphorus ylides are used widely, interest into the applications of sulfur ylides to synthetic problems has been stimulated by the work of Corey and Jautelat [10]. Sulfur ylides is generally performed α'-β elimination, Stevens rearrangement, and 2,3-sigmatropic rearrangement [11].

In 1947, Wittig observed that the treatment of tetramethylammonium bromide with phenyllithium in ether results in proton abstraction giving a nitrogen ylide [12].

Recently, Lloyd and coworkers have prepared a series of heteronium ylides of groups V and VI including selenium and tellurium [5,13,14]. Monoylides of arsenic are found thermally quite unstable materials [15–18].

Among the ylides, thiabenzene reported by Price and Suld [19] is of interest to chemists owing to

in situ generation and Stevens's rearrangement to thiopyrans [20–24]. This ylide has partly aromatic and ylide character.

Carbon atoms may form π bonds through pπ–pπ orbital overlaps with the first row atoms in the periodic table. While with the second row elements, such as phosphorus and sulfur, carbon does not generally form stable double bonds. This is due to the long distance between the parallel p orbitals involved, where little amount of overlap occurs. It was previously believed that the pπ–dπ bond is formed by the overlap between the filled p orbital from carbon with an empty d orbital from a second row atom. Also, it was previously assumed that the pπ–dπ bonding allows two canonical forms to be considered for phosphorus (C=P) and sulfur (C=S) ylides. Nevertheless, our calculations reveal no strong d-orbital participation in bonding.

Following our work on thiopyrans [25,26], here we take up the comparison of ylidic character and stability in heterocyclic benzenes.

METHOD OF CALCULATIONS

The Gaussian 98 system of programs is employed for the geometry optimizations on 1_X and 2_X at HF/6-311++G* and B3LYP/6-311++G* levels of theory [27–29]. The former optimized geometrical outputs are used as inputs for the B3LYB/6-311++G* calculations; obtaining more accurate values of activation electronic energies (E), enthalpies (H), and Gibbs free energies (G). To find energy minima, keyword "FOPT" is used. This keyword requests for a geometry optimization to be performed. The geometry will be adjusted until a stationary point on the potential surface is found. Here, the Berny algorithm is employed for all minimizations, using redundant internal coordinates [30]. For minimum state structures, only real frequency values are accepted. The calculations exhibit systematic errors and thus benefit from scaling. Thermodynamic functions obtained

through frequency calculations are multiplied by the scaling factor of 0.89 as suggested by Hout and Hehre [31] for HF/6-31G* and by the scaling factor of 0.99 as suggested by Rauhut and Pulay [32] for B3LYP/6-31G*. For heavy atoms, such as Te and Sb, the calculation was done with the McGrath and Curtiss basis set using "Extrabasis" keyword (heteroatoms are optimized using the LANL2DZ basis set) [33].

RESULTS AND DISCUSSION

In this paper, possibilities of homoaromaticity and ylide characters are investigated for the 6π-electrons containing heterocyclic benzenes that incorporate group 16 elements: oxabenzene (1_O), thiabenzene (1_S), selenabenzene (1_{Se}), tellurabenzene (1_{Te}), along with those incorporating group 15 elements: 1,1-dihydropyridinium (2_N), 1,1-dihydrophosphinium (2_P), 1,1-dihydroarsinium (2_{As}), and 1,1-dihydrostybinium (2_{Sb}) (Scheme 1). The electronic thermal energies, thermal enthalpies, and thermal free energies for 1_X and 2_X are calculated at various levels of theory (Fig. 1). To measure the extent of stability attained through homoaromaticity for 1_X and/or 2_X, the homodesmic method is employed [34]. This method, which is based on cyclic and acyclic reference system, is customarily used for measuring the stability of six-membered π-electron systems involving aromatic, homoaromatic, nonaromatic, and antiaromatic species. Here, the energies of starting materials 1_X and C_4H_6 are subtracted from their corresponding homodesmic products $1_{X'}$ (Scheme 2). Similarly, the energies of starting materials 2_X and C_4H_6 are subtracted from their corresponding homodesmic products $2_{X'}$. The trend of relative stability, ΔE_T, for 1_X series calculated at B3LYP/6-311++G* level is 1_S (15.0 kcal/mol) > 1_{Se} (14.6 kcal/mol) > 1_{Te} (11.7 kcal/mol) > 1_O (−4.6 kcal/mol). These results are consistent with the experimental data on the stability of related ylides
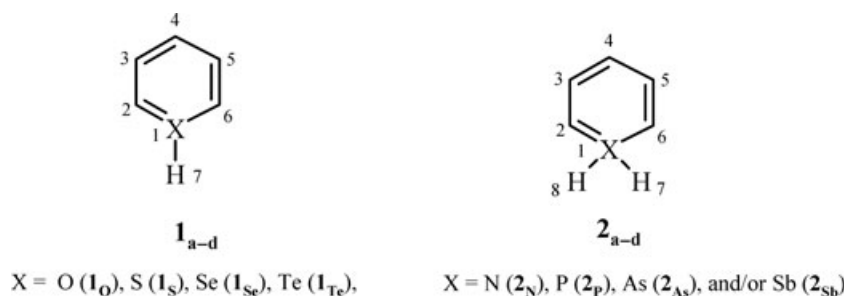
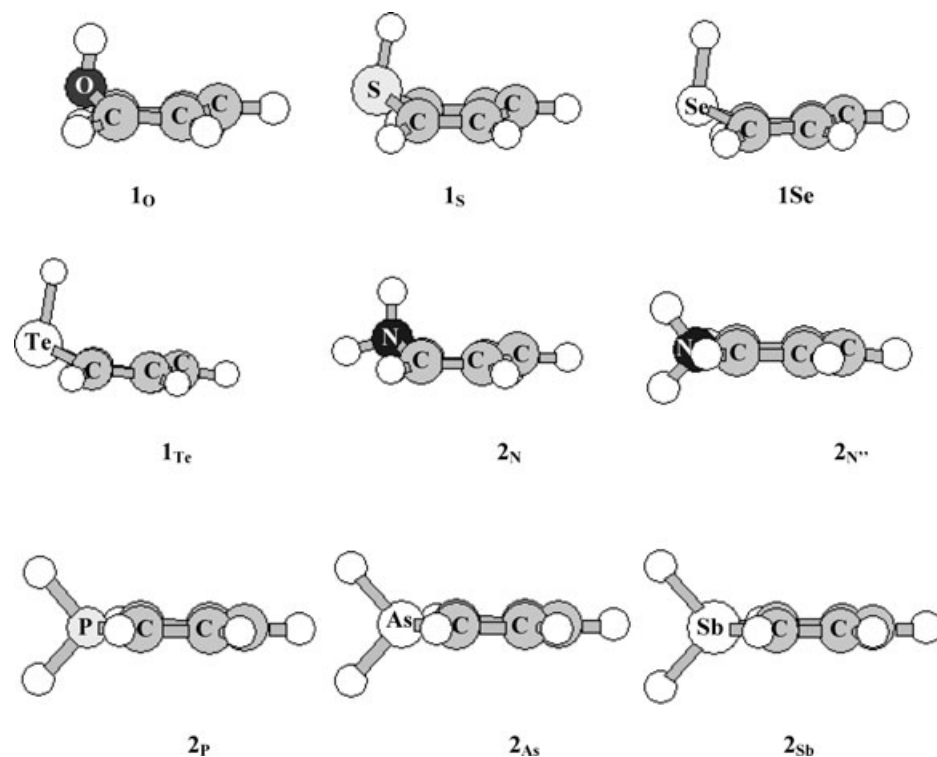SCHEME 1   Derivatives of heterocyclic benzenes 1_X and 2_X.

FIGURE 1   Optimized structures of heterocyclic benzenes 1_X and 2_X. White balls are hydrogen atoms.

[9]. Structure 1_O is the least stable for two reasons. First, placing a positive charge on oxygen, which is the most electronegative among group 16 elements, is the least desirable. Second, any contribution from a benzene form for 1_O contradicts the octet rule. The order of stability of $1_S, 1_{Se}$, and 1_{Te} is linearly proportional to the electronegativity (correlation factor, $R^2 = 0.997$), whereas indirectly proportional to the atomic volume and/or covalent radii of S, Se, and Te ($R^2 = 0.994$ and 0.907, respectively). In other words, the decrease of stability from 1_S toward 1_{Te} may be due to the decrease of the overlap between the heteroatom (S, Se, and Te) and the adjacent carbons.

The trend of relative stability, ΔE_T, for 2_X series calculated at B3LYP/6-311++G* level is 2_{As} (14.8 kcal/mol) > 2_P (14.1 kcal/mol) > 2_{Sb} (12.9 kcal/mol) > 2_N (12.9 kcal/mol). Excluding 2_N, this trend coincides with the inverse trend of atomic volume for group 15 elements: As (13.1) < P (17.0) < Sb (18.4). Apparently, the larger the heteroatom in the six-member ring, the less stable is the structure. A justification for the exclusion of 2_N
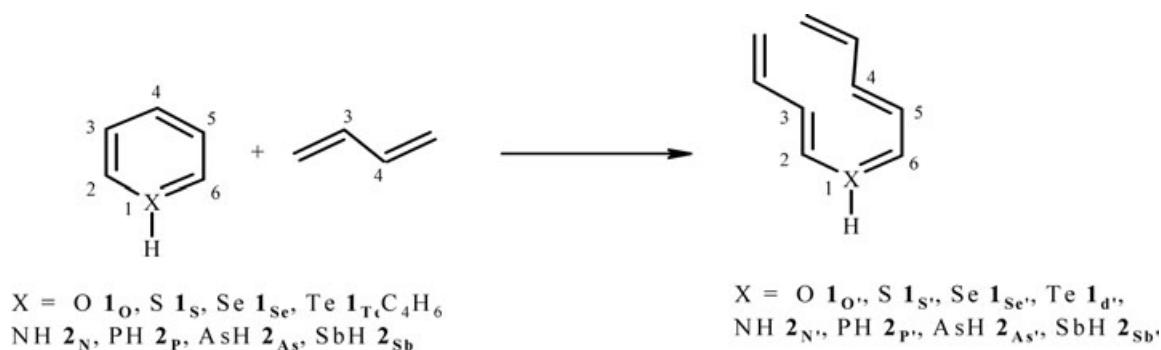
SCHEME 2   Homodesmic reaction between 1_X, 2_X and C_4H_6 forming the corresponding hypothetical products $1_{X'}$ or $2_{X'}$.
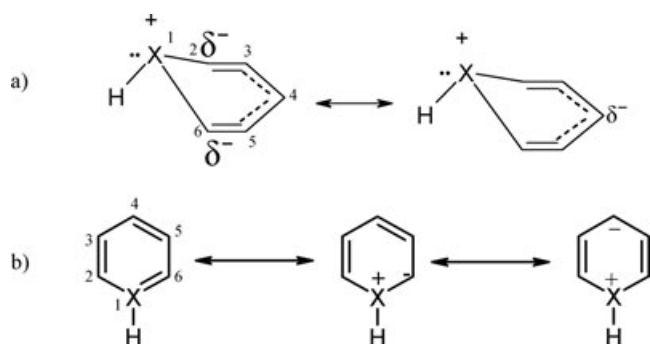
from the above energy trend is due to its instability for the reasons similar to those mentioned for 1_O. Obviously, placing a positive charge on nitrogen, which is the most electronegative among group 15 elements, destabilizes 2_N, whereas no stabilizing contribution is possible from a benzene-type canonical form for 2_N because nitrogen lacks d orbital in its valance electronic configuration, making such a canonical form go against the octet rule.

Except for 1_O, where the subtraction of the heat of formation of the reactants from that of the product is negative (Scheme 2), all the other compounds with 1_X and/or 2_X structures appear homoaromatic. This shows that the potential energy of their starting materials is lower than those of the corresponding products.

Change of basis set from 6-311++G* to LANL2DZ was necessary to accommodate heavy atoms (Te and Sb) in 1_{Te} and 2_{Sb}. Although such a change often leads to discrepancies, the stability orders appeared to follow the same trends regardless of the basis sets employed.

It is previously reported that because of $p\pi$–$d\pi$ bonding, two canonical forms can be suggested for phosphorus and sulfur (Scheme 3, ylide and ylene forms), but there is only one for nitrogen and oxygen. This leads to instability of nitrogen and oxygen ylides. However, the bond order calculations show a single bond for X_1–C_2, a double bond for C_2–C_3, and a quasi double bond for C_3–C_4 (Scheme 3a). Therefore, there is no $p\pi$–$d\pi$ bond between X_1–C_2 and/or X_1–C_6.

The HOMO–LUMO energy separation has been used as a simple indicator of kinetics stability [35]. A large HOMO–LUMO gap implies high kinetic stability and low chemical reactivity, because it is energetically favorable to add electrons to a high lying
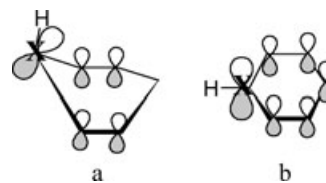

FIGURE 2   Two possibility constructions for 1_X. (a) Boat conformer and (b) planar conformer.

LUMO, to extract electrons from a low-lying HOMO, and so to form activated complex of any potential reaction [35]. A large HOMO–LUMO gap for 1_S, 2_{As}, and 2_P shows their high stability that confirmed the homodesmic procedure.

Compounds of 1_X and 2_X would have different proton substitutions on the ring. The charge on C_2, C_4, as well as C_6 is generally negative and on S_1, C_3, as well as C_5 is positive. The order of the Mulliken charge changes on X_1 is 1_{Te} (0.5) > 1_O (0.3) > 1_{Se} (0.2) > 1_S (0.1) and 2_{As} (0.6) > 2_N (0.4) > 2_{Sb} (0.3) > 2_P (0.1). This charge distribution on X_1 and adjacent carbon atoms confirms the extent of ylide character. The positive charge on X_1 atom in contrast to the negative charge on adjacent carbons increases from 1_S to 1_{Te} as well as from 2_P to 2_{Sb}. The charge on X_1 for 1_S and/or 2_P in the series is lowest and for 1_O and 2_N is highest. Therefore, 1_O and 2_N show the absolute ylide forms. The dipole moment also confirms the extent of ylide character. Hortmann and coworkers proposed the perfect resonance of negative charge on C_2 and C_4 (Scheme 3b) [36]. Nevertheless, the

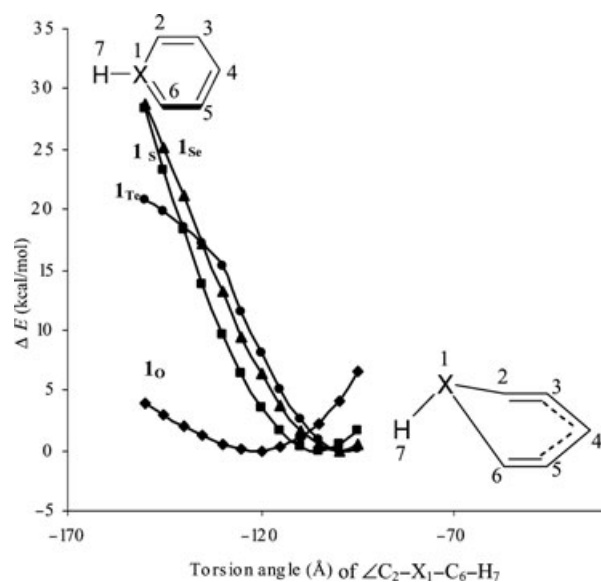**FIGURE 3**   Changes of inversion barrier energy (kcal/mol) through scanning the torsion angle (Å) of $\angle C_2$–X_1–C_6–H_7 for 1_X.

SCHEME 3   (a) Partial conjugation in nonplanar 1_X responsible for dispersing of negative charge on C_2 (C_6) and C_4. (b) Continuous conjugation in the planar 1_X responsible for dispersing of negative charge on all of the carbon atoms.

TABLE 1 Single Point Energy (with B3LYP/6-311++G* level, hartree) for Both Planar and Boat Conformer and Their Difference Energy (hartree and kcal/mol) of 1_X

Compound	Planar Form	Boat Form	$\Delta E(hartree)$	$\Delta E(kcal/mol)$
1_O	−269.213	−269.272	0.059	37.157
1_S	−592.182	−592.294	0.112	70.152
1_{Se}	−2595.505	−2595.622	0.116	73.062
1_{Te}	−201.986	−202.110	0.124	77.705

charge distribution on C_2 and C_4 shows partly resonance of negative charge (Scheme 3a).

The B3LYP/6-311++G* calculated geometrical parameters are presented. The bond lengths X_1–C_2 in contrast to C_2–C_3 decrease from 1_O to 1_S as well as from 2_N to 2_P. The bond lengths of 1_S, 1_{Se}, 1_{Te} as well as 2_P, 2_{As}, 2_{Sb} are not significantly changed. The order of bond length of X_1–H is $1_O < 1_S < 1_{Se} < 1_d$ and $2_N < 2_P < 2_{As} < 2_{Sb}$. These orders are reasonably related to more electropositivity of 1_{Te} and/or 2_{Sb}. The C_1–C_2–C_3 and C_2–X_1–C_6 in contrast to C_3–C_4–C_5 increase from 1_O to 1_{Te} as well as from 2_N to 2_{Sb}. The dihedral angles of C_2–X_1–C_6–C_5, X_1–C_2–C_3–C_4, and C_2–C_3–C_4–C_5 increase from 1_O to 1_{Te}. The order of dihedral angle C_2–X_1–C_6–C_5 (with the B3LYP/6-311++G* level) is 1_O 18.5 > 1_S 17.9 > 1_{Se} 15.4 > 1_{Te} 13.2 and 2_N −15.8 > $2_P = 2_{As} = 2_{Sb} = 0$. These orders show the C=X–C–C dihedral angle for 1_X is out of the plane and for 2_x is in the plane. Unshared electrons on sulfur and ylide character as well as low overlap between heteroatom and carbon orbitals may be the reason for the boat structure of 1_X (see Fig. 2). Conjugation of π-system in the ring tends to more planarity of 2_x. Interestingly, for two basis sets two conformers are found for 2_N (Fig. 1). Conformers 2_N and $2_{N''}$ are obtained with 6-311++G* and 6-31G* basis sets using the identical methods, respectively.

Compounds 1_X could be in two boat and planar conformers. In inversion process, p orbital on a sulfur atom containing an unshared electron becomes parallel to adjacent p orbitals on the carbons. This leads to a strong repulse interaction and diminish the conjugation of π electrons. Scanning of the torsion angle $\angle C_2$–X_1–C_6–C_5 was carried out to study the inversion barrier energy of the heteroatom atom for 1_X (Fig. 3). Also, single-point energies are calculated for both plane and boat conformers (Table 1). This energy difference may be related to inversion barrier. The order of difference in energies in kcal/mol is 1_O (37.2) < 1_S (70.1) < 1_{Se} (73.1) < 1_{Te} (77.7). This order shows a significant energy barrier between 1_O and others. The small size of oxygen may led to the lowest barrier energy of 1_O than 1_x. In contrast, compounds 2_x have just planar conformer (Scheme 3b). Con-

jugation of π-system in the ring tends to planarity. Therefore, planar conformer has six electrons, homoaromatic, and stable.

CONCLUSIONS

We have reasonably provided evidence of the bonding model for 1-heterocyclic benzenes 1_X and 2_X consistent with the experimental observation. The molecular structure of heterocyclic benzenes 1_X and 2_X is studied using ab initio calculations with the HF and DFT methods and 6-31G* as well as 6-311++G* basis sets. These compounds have 6π-electrons with homoaromatic and ylide character. Boat conformer for 1_X and planar conformer for 2_X are stable and have homoaromatic character. The stability of 1_X and 2_X is compared with a typical homodesmic reaction. The B3LYP/6-311++G* calculated stability of each series is as follows: $1_S > 1_{Se} > 1_{Te} > 1_O$ and $2_{As} > 2_P > 2_{Sb} > 2_N$. The order of inversion barrier energy of heteroatom for 1_X is $1_{Te} > 1_{Se} > 1_S > 1_O$.

SUPPLEMENTARY MATERIAL

Table 1 showing "sum of electronic and thermal energies (E), thermal enthalpies (H), thermal Gibbs free energies (G) in kcal/mol for heterocyclic benzenes 1_X and 2_X and other species occurring in homodesmic reaction" and Table 2 showing "energy difference between 1_X and 2_X and the corresponding homodesmic products: sum of electronic and thermal energies, ΔE_T; sum of electronic and thermal enthalpies, ΔH_T; sum of electronic and thermal free energies, ΔG_T" are available from the corresponding author on request.

REFERENCES

[1] Schollkopf, U. Angew Chem 1959, 71, 260.
[2] Musker, W. K. Fortschr Chem Forsch 1970, 14, 295–365.
[3] Belkin, Yu. V.; Polezhaeva, N. A. Russ Chem Rev 1981, 50, 481–497.
[4] Yaozeng, H.; Yanchang, S. Adv Organomet Chem 1982, 20, 115–157.

[5] Lloyd, D.; Singer, M. I. C. Chem Commun 1967, 390.
[6] Staudinger, H.; Meyer, J. Helv. Chim Acta 1919, 2, 635.
[7] Wittig, G.; Geissler, G. Justus Liebigs Ann Chem 1953, 580, 44.
[8] (a) Johnson, A. W. Ylide Chemistry; Academic Press: New York, 1966; (b) Bestmann H. J.; Zimmermann, R. Forfschr Chem Forsch 1971, 20, 1; (c) Kosolapoff, G. M.; Maier, L. (ed.); Organophosphorus Chemistry, Vol. 3; Wiley-lnterscience: New York, 1972; (d) Schmidbaur, H. Acc Chem Res 1975, 8, 62.
[9] Musker, W. K. J Chem Educ 1968, 46, 200.
[10] Corey, E. J. Jautelat, M. J Am Chem Soc 1967, 89, 3912.
[11] Wataru A. Acc Chem Res 1977, 10, 179.
[12] (a) Wittig, G.; Wetterling, M. Ann 1947, 557, 193; (b) Musker, W. K. 1968 J Chem Educ 45, 200.
[13] (a) Freeman, B. H.; Lloyd, D. Chem Commun 1970, 924; (b) Freeman, B. H.; Lloyd, D.; Singer, M. I. C. Tetrahedron 1972, 28, 343.
[14] Ernstbrunner, E.; Lloyd, D. Justus Liebigs Ann Chem 1971, 753, 196.
[15] Schmidbaur, H.; Tronich, W. Inorg Chem 1968, 7, 168.
[16] Schmidbaur, H.; Eberlein, J.; Richter, W. Chem Ber 1977, 110, 677.
[17] Richter, W.; Yamamoto, Y.; Schmidbaur, H. Chem Ber 1977, 110, 1312.
[18] Yamamoto, Y.; Schmidbaur, H. J Chem Soc, Chem Commun 1975, 110, 668.
[19] Suld, G.; Price, C. C. J Am Chem Soc 1961, 83, 1770.
[20] Price, C. C.; Horri, M.; Parasaran, T.; Polk, M. J Am Chem Soc 1963, 85, 2278.
[21] Price, C. C.; Follweiler, J.; Pirelahi, H.; Siskin, M. J Org Chem 1971, 36, 791.
[22] Price, C. C.; Pirelahi, H. J Org Chem 1972, 37, 1718.
[23] Pirelahi, H.; Abdoh, Y.; Hadjmirsadeghi, F.; Sagherichii, H. J Heterocycl Chem 1976, 13, 237.
[24] Pirelahi, H.; Abdoh, Y.; Afzali, A. Tetrahedron Lett 1976, 50, 4609–4612.
[25] Vessally, E.; Kavian, H.; Arshadi, S.; Pirelahi, H. J Mol Struct (Theochem) 2004, 678, 171–175.
[26] Kassaee, M. Z.; Vessally, E.; Pirelahi, H. Heteroatom Chem 2006, 17, 3
[27] Lee, C.; Yang, W.; Parr, R. G. Phys Rev B 1988, 37, 785.
[28] Becke, A. D. J Chem Phys 1993, 98, 5648.
[29] GAUSSIAN 98, Revision A. 6, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Znkrzewski, V. G.; Montgomery, G. A., Jr.; Startmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pamelli, C.; Adamo, G.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokoma, K.; Malick, D. K.; Rubuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslawski, J.; Oritz, J. V.; Stlefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Comperts, R.; Martin, R. L.; Fox, P. J.; Keith, T.; Al-laham, M. A.; Peng, C. Y.; Akkara, A. N.; Gonzales, C. G.; Combe, M. C.; Gill, P. M. W.; Johnson, B.; Chem, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1998.
[30] Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. J Comput Chem 1996, 17, 49.
[31] Hout, R. F., Jr.; Hehre, W. J. J Comput Chem 1982, 3, 234.
[32] Rauhut, G.; Pulay, P. J Phys Chem 1995, 99, 3093–3100.
[33] Schlegel, H. B.; Frisch, M. J. Int J Quantum Chem 1995, 54, 83.
[34] Cyranski, M. K.; Schleyer, P. R.; T. Krygowski, M.; Jiao, H.; Hohlneicher, G. Tetrahedron 2003, 59, 1657–1665.
[35] Manolopoulos, D. E.; May, J. C.; Down, S. E. Chem Phys Lett 1991, 181, 105.
[36] Hortmann, A. G.; Harris, R. L.; Miles, J. A. J Am Chem Soc 1974, 96, 6119.