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A DFT INVESTIGATION OF THE *ANTI*- AND *SYN*-FUSED ISOMERS OF DIFUROPYRIDINES, DIFUROPYRAZINES, AND THEIR DITHIENO ANALOGUES

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Abstract – Density functional theory calculations have been performed on the *anti*- and *syn*-isomers of a series of difuropyridines and difuropyrazines, as well as their dithieno analogues, and the results compared with those of the corresponding benzodifurans and benzodithiophenes. When the central ring in these systems was changed from benzene to pyridine and finally to pyrazine, the difference in the energy levels of the lowest unoccupied molecular orbitals (E_{LUMO}) of the *anti*- and *syn*-isomer became smaller, irrespective of the fused rings. Furthermore, the difference in the E_{LUMO} values of the furan- and thiophene-fused systems decreased as the central ring became increasingly electron deficient. In contrast, rather complicated trends were observed between the energy levels of the highest occupied molecular orbitals.

INTRODUCTION

Fused heteroaromatic compounds play an important role in the development of functional materials because they not only exhibit strong electron-donating and/or accepting characteristics but also display higher solubility and chemical stability properties than their hydrocarbon analogues in general.[1] From a structural perspective, it is noteworthy that fused heteroaromatic compounds can exist as different structural isomers with respect to the direction of their fused heterocyclic rings. Although the molecular structures of these isomers are similar, their properties can vary considerably. With this in mind, it could be possible to use these differences as an opportunity to exercise precise control over the properties of

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Dedicated to Professor Dr. LUTZ F. TIETZE on the occasion of his 75th birthday

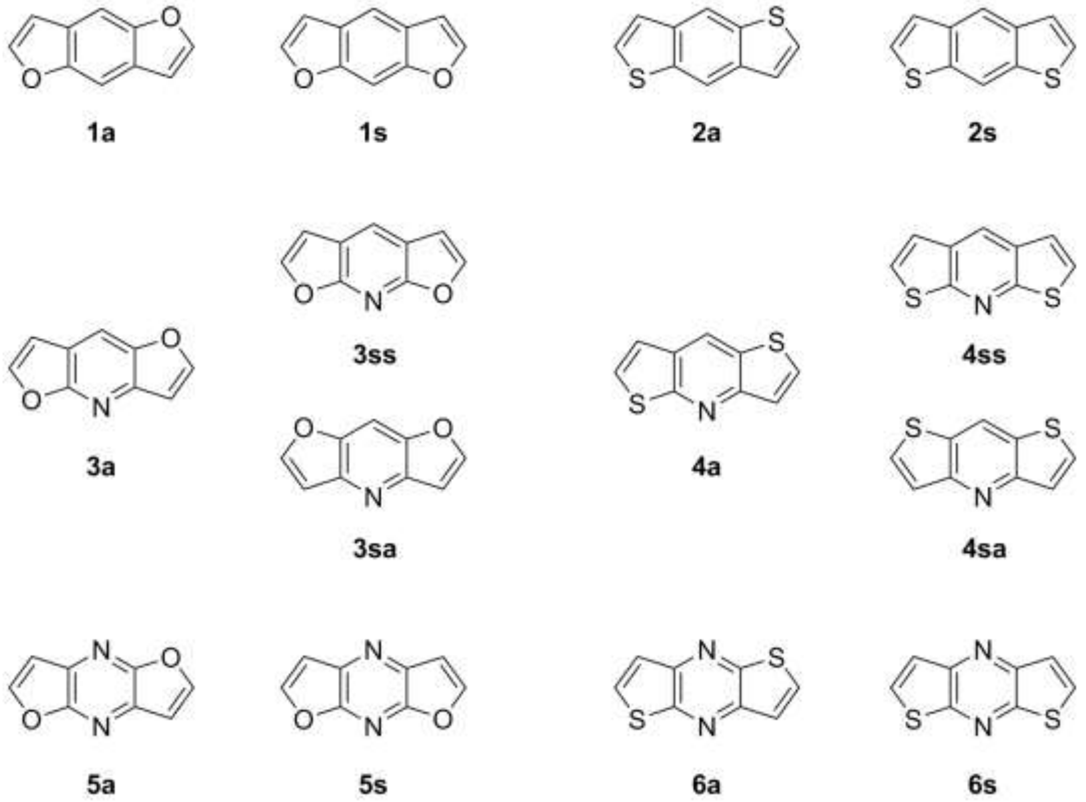

Chart 1. Benzodifurans (**1a** and **1s**), difuropyridines (**3a**, **3ss** and **3sa**), difuropyrazines (**5a** and **5s**) and their thiophene analogues (**2a**, **2s**, **4a**, **4ss**, **4sa**, **6a** and **6s**)

these materials.

Fused-thiophene compounds have been studied extensively as functional materials because of their strong electron-donating properties and their ability to form S···S contacts.[2–5] Considerable research efforts have also been directed towards the use of furan-fused compounds in material sciences.[6–9] Furan-fused compounds are considered to be inferior to the corresponding thiophene-fused systems with respect to their electronic properties (i.e., ability to form intermolecular interactions, conductivity and mobility). For example, the "hard" character of the furan oxygen prevents it from participating in the formation of specific intermolecular interactions in the same way as the "soft" sulfur atom of thiophene, which can form S···S interactions. Furan-fused compounds, however, are intrinsically more fluorescent than the corresponding thiophene-fused systems because they lack the heavy atom effect.[10] These differences in the properties of furan- and thiophene-fused compounds mean that they could potentially be used in different applications to take advantages of their unique properties. However, the precise nature of the differences between furan- and thiophene-fused compounds remains unclear and further research is therefore required to enhance our collective understanding of these systems.

Benzodifurans (BDFs) are one of the simplest classes of furan-fused compounds, and compounds belonging to this class can exist as structural isomers with respect to the direction of their furan rings. The two different isomers of BDFs, **1a** and **1s** (Chart 1), are referred to as the *anti*- and *syn*-isomers, respectively. In the *anti*-isomer **1a**, the two furan rings are fused in an *anti*-parallel manner, whereas the rings in the corresponding *syn*-isomer **1s** are fused in a parallel manner. We previously reported the redox potentials, electronic absorption/emission spectra and fluorescence quantum yields of **1a** and **1s** and found that their behaviors were significantly different from those of their thiophene analogues, **2a** and **2s** (vide infra).[11] Whilst the results of our previous study revealed that there are significant differences between these simple furan- and thiophene-fused compounds, it still remains unclear whether these differences are common to more complicated molecules from these classes.

In this study, we have conducted a theoretical investigation on the *anti*- and *syn*-isomers of a series of difuropyridines (**3a**, **3ss** and **3sa**) and difuropyrazines (**5a** and **5s**), as well as their thiophene analogues (**4a**, **4ss**, **4sa**, **6a** and **6s**). The aim of this study was to develop a better understanding of the way in which the energy levels of the highest occupied molecular orbitals (HOMOs), E_{HOMO}, and the lowest unoccupied molecular orbitals (LUMOs), E_{LUMO}, changed when the electronic characteristics of the central ring changed for the different isomers. We also examined the differences in the E_{HOMO} and E_{LUMO} values of the *anti*- and *syn*-isomers of the different compounds [i.e., ΔE_{HOMO}(*anti*/*syn*) and ΔE_{LUMO}(*anti*/*syn*), respectively]. Lastly, we measure the differences between the E_{HOMO} and E_{LUMO} values of the furan-fused molecules and their thiophene analogues [i.e., ΔE_{HOMO}(F/T) and ΔE_{LUMO}(F/T), respectively]. Although the synthesis and reactivity of furopyridines have been reviewed previously,[12] there have been very few reports pertaining to the properties of extended π-systems such as a difuropyridines.

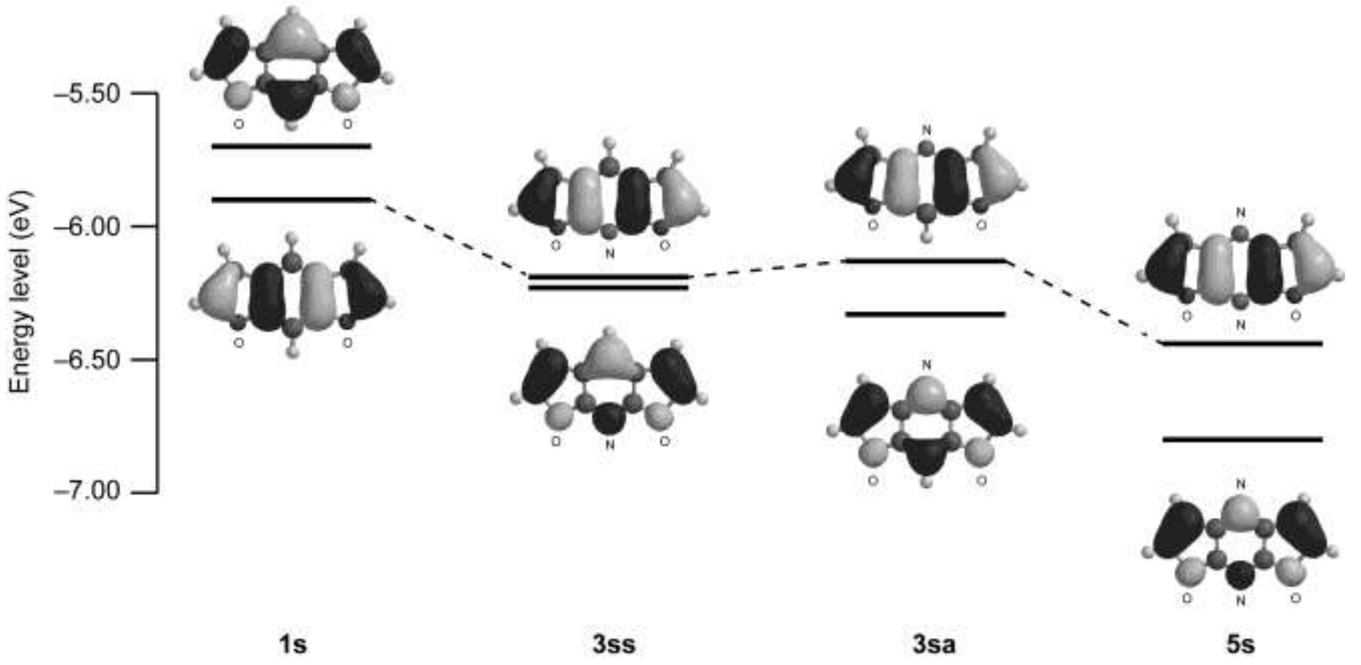

Figure 1. Diagram of E_{HOMO} and $E_{\mathrm{HOMO-1}}$ of **1s**, **3ss**, **3sa**, and **5s**

RESULTS AND DISCUSSION

The geometries of compounds **1a–6a** and **1s–6s** were optimized by density functional theory (DFT) at the B3LYP/6-31(d,p) level. The E_{HOMO}, $E_{\text{HOMO–1}}$ (selected) and E_{LUMO} values of the different compounds are shown in Table 1. A comparison of the E_{HOMO} and E_{LUMO} values for the different series (i.e., **1a**/**3a**/**5a**, **1s**/**3ss**/**3sa**/**5s**, **2a**/**4a**/**6a** and **2s**/**4ss**/**4sa**/**6s** – shown vertically in Chart 1) revealed that the energy levels became progressively lower as the central ring was changed from benzene to pyridine and finally to pyrazine. This decrease in the energy was attributed to the central ring becoming increasingly electron-deficient following the inclusion of one and then two nitrogen atoms. It was envisaged that these changes in the electronic characteristics of the central ring would have a significant impact on the electron-donating and electron-accepting properties of the entire system fused system. Notably, molecular orbitals (MOs) consisting of a linear combination of atomic orbitals (AOs), which were similar to those of the HOMO in **1s**, were considered as the HOMO–1 in **3ss**, **3sa** and **4s**, whilst MO similar to the HOMO–1 of **1s** was considered to be the HOMO in these molecules (Figure 1). This difference was attributed to the AO coefficients at the 9- and 10-positions of the HOMO–1 of **1s** being zero. This meant that the energy

Table 1. The HOMO, HOMO–1 (selected) and LUMO energy levels of **1a**–**6a** and **1s**–**6s**, which were calculated using DFT at the B3LYP/6-31G(d,p) levels. The gaps between the energy levels are also shown.

Compd	E_{HOMO}	$E_{\text{HOMO–1}}$	E_{LUMO}	ΔE_{HOMO} (*anti*/*syn*)	ΔE_{LUMO} (*anti*/*syn*)	ΔE_{HOMO} (F/T)	ΔE_{LUMO} (F/T)
1a	–5.55		–0.82				
1s	–5.70	–5.90	–0.70	0.15 (0.35)[a]	–0.12		
3a	–5.93		–1.30				
3ss	–6.19	–6.23	–1.19	0.26	–0.11		
3sa	–6.13	–6.33	–1.23	0.20	–0.07		
5a	–6.26		–1.88				
5s	–6.44	–6.80	–1.81	0.18	–0.07		
2a	–5.48		–1.10			–0.07	0.28
2s	–5.50		–0.90	0.02	–0.20	–0.20 (–0.40)[b]	0.20
4a	–5.89		–1.48			–0.04	0.18
4ss	–5.91		–1.32	0.02	–0.16	–0.28	0.13
4sa	–5.96		–1.38	0.07	–0.10	–0.17	0.15
6a	–6.25		–1.98			–0.01	0.10
6s	–6.32		–1.90	0.07	–0.08	–0.12	0.09

[a] The gap between E_{HOMO}(**1a**) and $E_{\text{HOMO–1}}$(**1s**). [b] The gap between $E_{\text{HOMO–1}}$(**1s**) and E_{HOMO} (**2s**).

level of this orbital was influenced to a much lesser extent by the introduction of nitrogen atoms to the core ring than that of the HOMO of **1s**, where the AO coefficients at the 9- and 10-positions were significant values. For a fair comparison, HOMO–1 of **1s** was often compared with HOMOs of **3ss**, **3sa** and **5s** in this study.

A comparison of the *anti*- and *syn*-isomers of the different compounds revealed that the ΔE_{HOMO}(*anti*/*syn*) values were greater than zero in all cases. This result indicated that all of the *anti*-isomers evaluated in the current study were more electron-donating in character than the corresponding *syn*-isomers. Furthermore, all of the ΔE_{LUMO}(*anti*/*syn*) values were determined to be negative, which confirmed that the *anti*-isomers were more electron-accepting in character than the *syn*-isomers. These results can be readily explained in terms of the electronic theory of organic chemistry. The π-conjugated system would be extended over a greater number of alternating single and double bonds in the *anti*-isomer compared with the *syn* isomer, as indicated by the black lines for the different canonical structures (Chart 2). The greater degree of conjugation in the *anti*-isomer would make it lower in energy than the corresponding *syn*-isomer. This suggestion was supported experimentally by the first oxidation potential (onset) of **1a**, which was determined to be +0.92 V and slightly less than that of **1s** (+1.00 V).[11]

1a **1s**

Chart 2

A large energy gap (0.15 eV) was observed between the E_{HOMO} values of **1a** and **1s**, ΔE_{HOMO}(**1a**/**1s**), which is a unique feature of BDFs that has never been reported in the other benzodichalcogenophenes. In fact, the ΔE_{HOMO}(**2a**/**2s**) value was only 0.02 eV at the same calculation level, and similar results have been reported for benzodiselenophenes and benzoditellurophene.[11] Large energy gaps were also observed in the other furan-fused molecules evaluated in this study. For example, the E_{HOMO}(**3a**/**3ss**), E_{HOMO}(**3a**/**3sa**) and E_{HOMO}(**5a**/**5s**) values were determined to be 0.26, 0.20 and 0.18 eV, respectively. There is no obvious trend between these values and ΔE_{HOMO}(**1a**/**1s**). This is probably because the HOMOs of **3ss**, **3sa**, and **5s** consist of a linear combination of AOs which is rather different from that of the HOMO of **1s** but similar to that of its HOMO–1. Indeed, when these values are compared with the energy gap between E_{HOMO}(**1a**) and $E_{\mathrm{HOMO-1}}$(**1s**), 0.35 eV, the size of the energy gap in these systems was dependent on the electronic properties of the central ring, with the energy gap increasing in size as the central ring became more electron deficient. In contrast, the energy gaps of the corresponding thiophene-fused analogues were small at 0.02, 0.07 and 0.07 eV for ΔE_{HOMO}(**4a**/**4ss**), ΔE_{HOMO}(**4a**/**4sa**) and ΔE_{HOMO}(**6a**/**6s**), respectively. It is

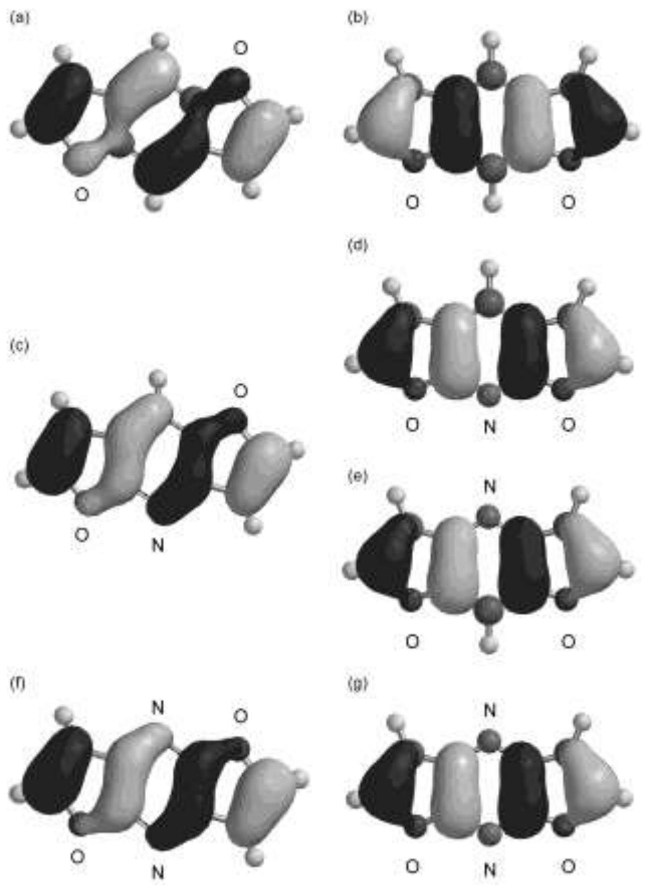

Figure 2. HOMOs of (a) **1a**, (c) **3a**, (d) **3ss**, (e) **3sa**, (f) **5a**, and (g) **5s** and HOMO–1s of (b) **1s**. Oxygen and nitrogen atoms are designated.

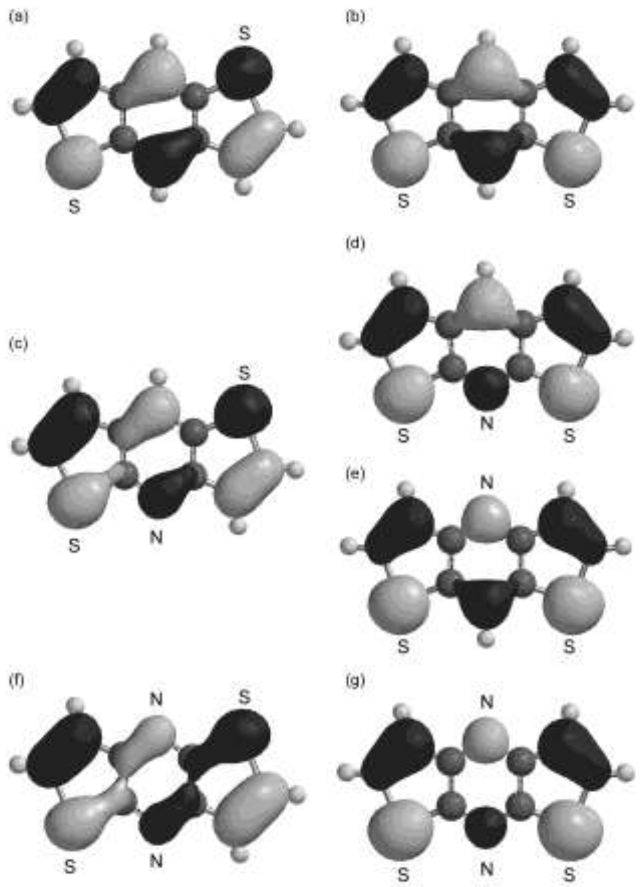

Figure 3. HOMOs of (a) **2a**, (b) **2s**, (c) **4a**, (d) **4ss**, (e) **4sa**, (f) **6a**, and (g) **6s**. Nitrogen and sulfur atoms are designated.

noteworthy, that the ΔE_{HOMO}(*anti*/*syn*) values of the thiophene-fused molecules also increased as the central ring became increasingly electron deficient. As shown in Figures 2 and 3, the HOMOs of the furan-fused molecules (except **1s**, for which the HOMO–1 is employed) were different from those of the corresponding thiophene-fused systems for the both *syn*- and *anti*-isomers, giving rise to no similar tendency in the E_{HOMO} values.

In contrast, a common behavior was observed in comparison of the ΔE_{LUMO}(*anti*/*syn*) values. The ΔE_{LUMO}(*anti*/*syn*) values were all negative; for example, the ΔE_{LUMO}(**1a**/**1s**), ΔE_{LUMO}(**3a**/**3ss**), ΔE_{LUMO}(**3a**/**3sa**) and ΔE_{LUMO}(**5a**/**5s**) values were determined to be –0.12, –0.11, –0.07 and –0.07 eV, respectively, whilst the ΔE_{LUMO}(**2a**/**2s**), ΔE_{LUMO}(**4a**/**4ss**), ΔE_{LUMO}(**4a**/**4sa**) and ΔE_{LUMO}(**6a**/**6s**) were determined to be –0.20, –0.16, –0.10 and –0.08, respectively. In both of these series, the size of the energy gap decreased as the central ring became increasingly electron deficient. As shown in Figure 4, the AO coefficients of the central ring increased as the ring was changed from benzene to pyridine and finally to pyrazine, whilst those of the oxygen and C_{β} atoms decreased. The electronic characteristics of the

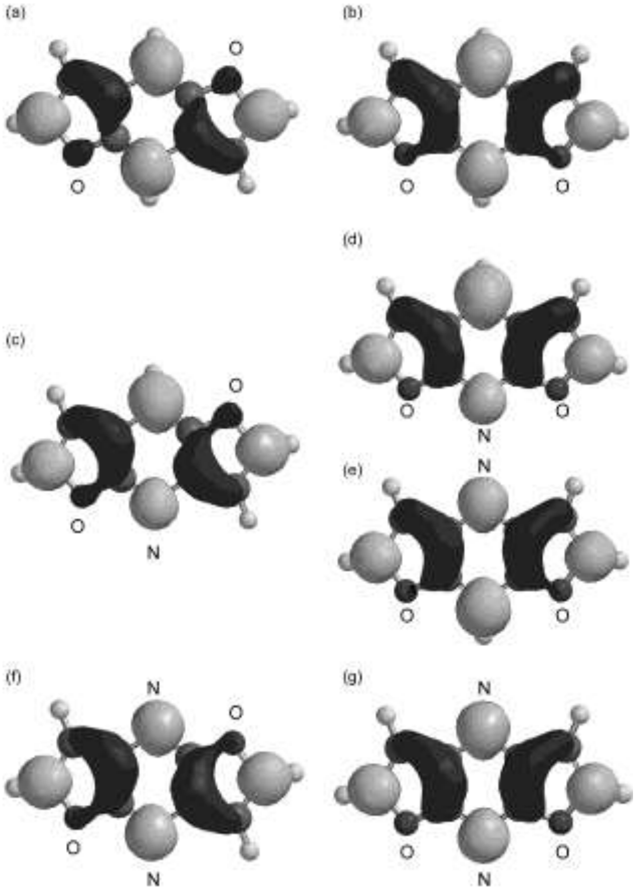

Figure 4. LUMOs of (a) **1a**, (b) **1s**, (c) **3a**, (d) **3ss**, (e) **3sa**, (f) **5a**, and (g) **5s**. Nitrogen and sulfur atoms are designated.

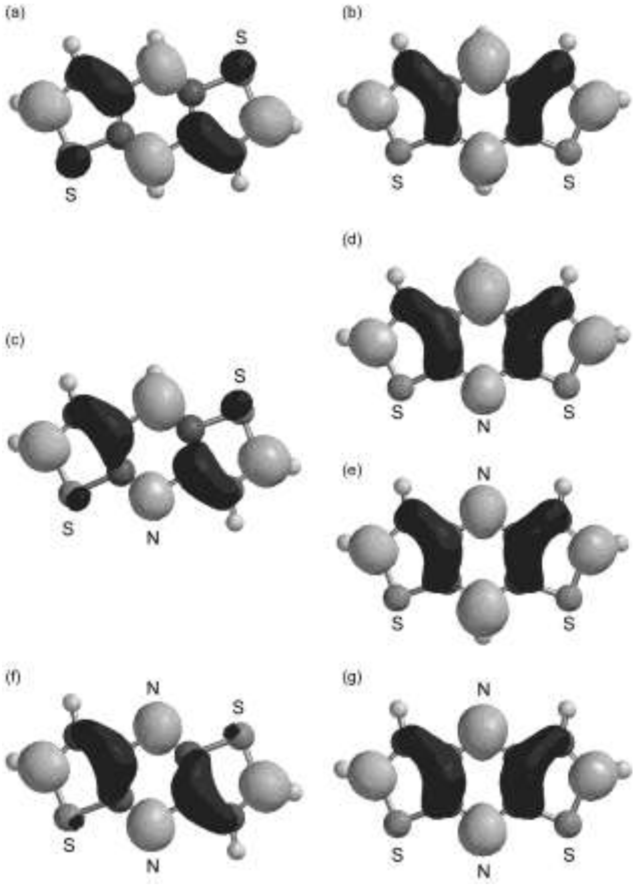

Figure 5. LUMOs of (a) **2a**, (b) **2s**, (c) **4a**, (d) **4ss**, (e) **4sa**, (f) **6a**, and (g) **6s**. Nitrogen and sulfur atoms are designated.

central ring therefore made a significant contribution to lowering the energy levels of the LUMOs. The MOs of thiophene-fused molecules varied in a similar manner, as shown in Figure 5.

It is noteworthy that all of the ΔE_{HOMO}(F/T) values determined in the current study were negative, whilst all of the ΔE_{LUMO}(F/T) values were positive (Table 1). These results indicated that the furan-fused molecules were less electron-donating and less electron-accepting in character than the corresponding thiophene-fused systems. These results were therefore consistent with those of the ionization potentials of benzofuran (8.37 eV) and benzothiophene (8.13 eV).[13,14] These differences could be attributed to the differences in the electronegativities of the two heteroatoms (O: 3.5, S: 2.6), as well as differences in the contributions made by their AOs to the HOMOs and LUMOs of the fused systems. Indeed, as shown in Figures 2–5, the AO coefficients on the oxygen atoms of the furan-fused molecules were smaller than those on the sulfur atoms of the corresponding thiophene-fused systems. This result indicated that the oxygen atoms were making a smaller contribution to increasing the E_{HOMO} and lowering the E_{LUMO} values in the furan-fused molecules compared with the sulfur atoms in the corresponding thiophene-fused systems. A comparison of the ΔE_{LUMO}(**1a**/**2a**), ΔE_{LUMO}(**3a**/**4a**) and ΔE_{LUMO}(**5a**/**6a**) values revealed that the energy gap became smaller when the central ring was changed from benzene to pyridine and finally to pyrazine. A similar tendency was also observed for ΔE_{LUMO}(**1s**/**2s**), ΔE_{LUMO}(**3s**/**4ss**), ΔE_{LUMO}(**3s**/**4sa**) and ΔE_{LUMO}(**5s**/**6s**) values. Once again, this effect can be attributed to the electron-deficient properties of the central ring leading to an increase in the AO coefficients on the LUMO of the central ring. The fused heterocyclic rings in these compounds would consequently make a much smaller contribution to the energy of the LUMO.

A comparison of the ΔE_{HOMO}(**1a**/**2a**), ΔE_{HOMO}(**3a**/**4a**) and ΔE_{HOMO}(**5a**/**6a**) values was similar to that of the ΔE_{LUMO}(F/T). When the central ring in these systems was changed from benzene to pyridine and finally to pyrazine, the energy gaps increased. In contrast, there was no trend followed by the ΔE_{HOMO}(F/T) of the *syn*-isomers. But once again, when the $E_{\mathrm{HOMO-1}}$(**1s**) was employed instead of the E_{HOMO}(**1s**), the energy gaps, $\Delta E'$(**1s**/**2s**) [= $E_{\mathrm{HOMO-1}}$(**1s**) – E_{HOMO}(**2s**)], ΔE_{HOMO}(**3ss**/**4s**), ΔE_{HOMO}(**3sa**/**4s**) and ΔE_{HOMO}(**5s**/**6s**), decreased in this order. As shown in Figures 2–5, the AO coefficients of the hetero atoms are larger in the HOMOs than in the LUMOs. Nevertheless, the ΔE_{HOMO}(F/T), where $\Delta E'$(**1s**/**2s**) was employed instead of ΔE_{HOMO}(**1s**/**2s**), values progressively decreased when the central ring in these systems was changed from benzene to pyridine and finally to pyrazine as seen in the ΔE_{LUMO}(F/T) values.

In conclusion, we have shown that the ΔE_{LUMO}(*anti*/*syn*) and ΔE_{LUMO}(F/T) values of a series of different furan- and thiophene-fused heterocycles decreased in order of BDFs/benzodithiophenes (BDTs) > difuropyridines/dithienopyridines > difuropyrazines/dithienopyrazines. This trend can be attributed to the AO coefficients of the furan- and thiophene-fused rings become progressively smaller as the central ring became increasingly electron deficient. In contrast, the differences in the ΔE_{HOMO}(F/T) values of the different systems did not appear to follow a common trend. The ΔE_{HOMO}(*anti*/*syn*) values of the difuropyridines and difuropyrazines were larger than those of the corresponding dithienopyridines and dithienopyrazines, as noted for the BDFs and BDTs. These results could provide important guidelines for the design of functional electron-accepting materials based of fused-heteroaromatic compounds.

EXPERIMENTAL

B3LYP calculations were performed with the Spartan '04 software package using the 6-31G(d,p) basis set. In all of the calculations, *C*2*v* symmetry was assumed for **1a**, **2a**, **5a** and **6a**; *C*2*h* symmetry was assumed for **1s**, **2s**, **3ss**, **3sa**, **4ss**, **4sa**, **5s** and **6s**; and *C*1 symmetry was assumed for **3a** and **4a**.

ACKNOWLEDGEMENTS

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14. In contrast, ionization potentials of furan and thiophene themselves are rather close, which are 8.89 and 9.00 eV, respectively (ref 13).