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Aromaticity of dihetero analogues of pentalene dianion. X-Ray and ab initio studies of eight methyl furo[3,2-*b*]pyrrole-5-carboxylate derivatives and five methyl furo[2,3-*b*]pyrrole-5-carboxylate derivatives

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Abstract—The crystal and molecular structures of eight methyl furo[3,2-*b*]pyrrole-5-carboxylate derivatives (4*H*; 2,3-dimethyl-4*H*; 2-formyl-4*H*; 2-(4-chloro-2-methyl)phenoxy-4-methyl; 4-benzyl-2-methyl; 4-benzyl-2,3-dimethyl; 4-benzyl-2-formyl; 4-benzyl-2-(4-chloro-2-methyl)phenoxy and five methyl furo[2,3-*b*]pyrrole-5-carboxylate derivatives (2-formyl-6*H*, 2-formyl-6-methyl, 2-cyano-6-methyl, 6-benzyl-2-formyl-, 6-benzyl-2-cyano) have been solved by X-ray diffraction and supplemented by ab initio RHF/6-311+G** and B3LYP/6-311+G** calculations. The molecular geometries of the furo[3,2-*b*]pyrrole and furo[2,3-*b*]pyrrole fragment were used to study the aromatic character of these systems leading to the conclusion that the aromaticity of the rings practically does not depend on the nature of the atom in a neighbouring ring if a similar topological pattern is concerned. In line with the observed stability of the systems, the aromaticity of the furo[2,3-*b*]pyrrole derivatives is definitely smaller in comparison with the structural isomer the furo[3,2-*b*]pyrrole, implying that the most important factor which determines the aromatic character of a moiety is of topological nature. The stability and aromaticity of the compounds reveal a strong dependence on the substituent effect, much stronger than in the case of benzene derivatives.

Aromaticity plays one of the most fundamental roles in modern organic chemistry,[1,2] especially in the chemistry of heterocyclic π-electron systems.[1–5] In the last few decades, it has proved its leading position not only for qualitative aspects but also for quantitative applications.[1,2,6] The concept is usually defined in terms of energetic, magnetic and geometric criteria[1,2,7] which need not always be equivalent.[5,6,8,9] Recently, Schleyer et al.[10] have studied the aromatic character of furo-furanes, thieno-thiophenes, benzofurans and benzo-thiophenes, and concluded that there need not be any direct relationship between the thermodynamic stability of the heterobicyclic isomers and their aromaticity. The analyses were then followed by Novak.[11] Both these theoretical studies have importantly revealed, that [1,4] endosubstituted thienothiophenes and furofurans are slightly more aromatic than their [1,6] analogues, in line with the Gimarc topological charge stabilization rule.[12] The title systems, derivatives of furo[3,2-*b*]pyrrole and furo[2,3-*b*]pyrrole are interesting, experimentally accessible model systems, which can substantially enrich the knowledge based on theoretical investigations[10–13] on aromaticity and stability of heterobicyclic systems. According to the Hückel 4N+2 rule[14] both systems should be considered as aromatic.

The purpose of this paper is to study quantitatively the aromaticity of the π-electron rings in eight furo[3,2-*b*]pyrrole[15–17] and five newly-synthesised furo[2,3-*b*]pyrrole derivatives[18] in their monocyclic fragments in function of the substitution. The study is based on the experimentally (by X-ray) determined geometry of thirteen derivatives enriched by ab initio RHF and DFT calculations for a few model compounds. To our knowledge[19] no furo[2,3-*b*]pyrrole systems have been structurally investigated (by means of X-ray studies) and the crystal structure of only one derivative of furo[3,2-*b*]pyrrole[20] has been reported so far.

The aromatic character of the systems is studied by use of the geometry-based Harmonic Oscillator Model of Aromaticity (HOMA)[21,22] and magnetic index Nucleus Independent Chemical Shift (NICS).[23] Both models have been very successful in describing the aromatic character of many diverse π-electron systems[2,6,24] especially in the case of heterocyclic systems.[2,24] It is expected that both

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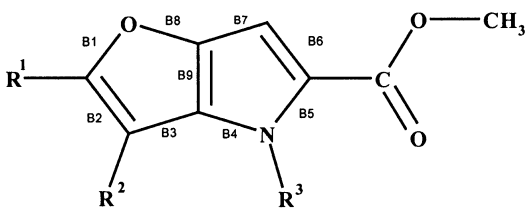
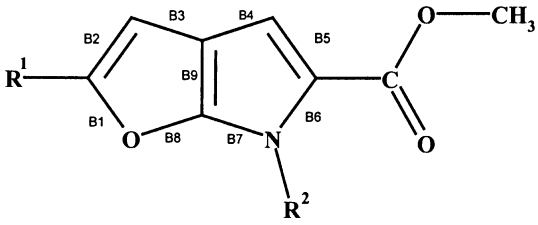
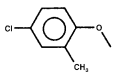
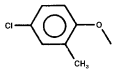




Compound	R^1	R^2	R^3	Compound	R^1	R^2
(1)	**H**	**H**	**H**	**(9)**	**CHO**	**H**
(2)	**CH_3**	**CH_3**	**H**	**(10)**	**CHO**	**CH_3**
(3)	**CHO**	**H**	**H**	**(11)**	**CN**	**CH_3**
(4)		**H**	**CH_3**	**(12)**	**CHO**	**CH_2-Ph**
(5)	**CH_3**	**H**	**CH_2-Ph**	**(13)**	**CN**	**CH_2-Ph**
(6)	**CH_3**	**CH_3**	**CH_2-Ph**			
(7)	**CHO**	**H**	**CH_2-Ph**			
(8)		**H**	**CH_2-Ph**			

Scheme 1. The studied systems with labelling of selected bonds.

models may be very efficient in the accurate deduction of stabilisation energies due to cyclic electron delocalisation.[25]

1. Results and discussion

The molecular geometries of eight furo[3,2-*b*]pyrrole derivatives, (**1**)–(**8**) and of five furo[2,3-*b*]pyrrole derivatives, (**9**)–(**13**), shown in Scheme 1, allowed us to estimate the aromaticity index HOMA (Eq. 1).[26]

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum(R_{\mathrm{opt}} - R_i)^2 \qquad (1)$$

Where n is the number of bonds taken into account; α is a normalisation constant (fixed to give HOMA=0 for a model non-aromatic system[21] and 1 for the system with all bonds equal to the optimal value R_{opt}—which is assumed to be

Table 1. Aromaticity of the systems (**1**)–(**13**). HOMA given as total values, for pyrrole and furan fragment, respectively. The values based on B3LYP/6-311+G** and HF/6-311+G** are given in bold and in italics, respectively. The values based on experimental data are given in normal type. The NICS values computed at GIAO-HF/6-31+G* are given in parentheses

System	HOMA [total]	HOMA [pyrrole]	HOMA [furan]	System	HOMA [total]	HOMA [pyrrole]	HOMA [furan]
(**1**)	0.450	0.933 (−15.4)	0.063 (−10.3)	(**8**)	0.385	0.887	−0.028
(**1**)	**0.515**	**0.912** (**−15.8**)	**0.215** (**−10.8**)	(**9**)	0.409	0.82 (−13.3)	0.103 (−9.3)
(**1**)	*0.58*	*0.892* (*−15.6*)	*0.312* (*−10.8*)	(**9**)	**0.451**	**0.832** (−13.8)	**0.180** (−9.8)
(**2**)	0.398	0.908 (−15.4)	−0.014 (−9.2)	(**9**)	*0.529*	*0.794* (*−13.7*)	*0.335* (*−9.8*)
(**2**)	**0.457**	**0.909** (**−15.8**)	**0.114** (**−9.6**)	(**10**)	0.410	0.811 (−13.8)	0.118 (−9.2)
(**2**)	*0.539*	*0.887* (*−15.6*)	*0.233* (*−9.6*)	(**10**)	**0.438**	**0.816** (−14.1)	**0.171** (−9.6)
(**3**)	0.53	0.959 (−15.4)	0.195 (−10.7)	(**10**)	*0.529*	*0.806* (*−14.1*)	*0.326* (*−9.7*)
(**3**)	**0.576**	**0.915** (**−15.6**)	**0.32** (**−11.3**)	(**11**)	0.411	0.834 (−14.2)	0.098 (−10.4)
(**3**)	*0.66*	*0.899* (*−15.3*)	*0.456* (*−11.1*)	(**11**)	**0.392**	**0.826** (**−14.4**)	**0.080** (**−10.8**)
(**4**)	0.395	0.926	−0.03	(**11**)	*0.494*	*0.802* (*−14.4*)	*0.261* (*−10.8*)
(**5**)	0.456	0.892	0.104	(**12**)	0.44	0.837	0.147
(**6**)	0.426	0.906	0.046	(**13**)	0.418	0.843	0.087
(**7**)[a]	0.527	0.925	0.223				

[a] Mean value.

Table 2. Aromaticity of the systems (**14**)–(**19**). HOMA given as total values, for pyrrole and furan fragment, respectively. The values based on B3LYP/6-311+G** and HF/6-311+G** are given in bold and in italics. The NICS values computed at GIAO-HF/6-31+G* are given in parentheses

System	HOMA [total]	HOMA [pyrrole]	HOMA [furane]	System	HOMA [total]	HOMA [pyrrole]	HOMA [furane]
(**14**)	**0.827**	**0.843** (−14.7)	–	(**17**)	**0.740**	**0.766** (**−13.8**)	–
(**14**)	*0.805*	*0.813* (*−14.3*)	–	(17)	*0.689*	*0.706* (*−13.5*)	–
(**15**)	**0.129**	–	**0.201** (**−11.9**)	(**18**)	**−0.006**	–	**0.076** (**−11.0**)
(**15**)	*0.255*	–	*0.259* (*−11.8*)	(18)	*0.093*	–	*0.117* (*−10.9*)
(**16**)	**0.483**	**0.874** (**−15.4**)	**0.193** (**−11.3**)	(**19**)	**0.349**	**0.776** (**−14.4**)	**0.044** (**−10.4**)
(**16**)	*0.535*	*0.807* (*−15.1*)	*0.289* (*−11.2*)	(19)	*0.378*	*0.683* (*−14.0*)	*0.122* (*−10.3*)

realised when full delocalization of π-electrons occurs) and R_i stands for a running bond length.[26]

The molecular geometries were also used for a single point computation of Nucleus Independent Chemical Shifts (NICS).[23] The NICS is defined[23] as a negative value of the absolute shielding computed at a ring centre (or some other interesting point[24] of the system). Rings with negative NICS values qualify as aromatic, and the more negative NICS, the more aromatic are the rings. Table 1 presents aromaticity indices for (**1**)–(**13**) based on their experimental geometries and supplemented by computational-based data for selected systems.

For comparison also the parent unsubstituted systems: pyrrolo[3,2-*b*]pyrrole (**14**), furo[3,2-*b*]furan (**15**), furo[3,2-*b*]pyrrole (**16**), pyrrolo[2,3-*b*]pyrrole (**17**), furo[2,3-*b*]furan (**18**) and furo[2,3-*b*]pyrrole (**19**) have been optimised at B3LYP/6-311+G** and HF/6-311+G** level of theory. The aromaticity of these systems is shown in Table 2.

The furopyrrole moiety is a non-alternant system and hence, most probably, considerable differences in measured and calculated geometric parameters are observed. Since the DFT parameters are much closer to the experimental ones, these data were mostly used in further processing. Importantly, the NICS values computed for the high precision experimental geometries are very close (with a maximum difference not exceeding 0.6 ppm) to those calculated using ab initio optimised geometries (RHF and B3LYP). Moreover, the difference in the case of ab initio obtained structures is even smaller ($\Delta \leq 0.4$ ppm). This finding is particularly interesting in comparison with rather sensitive values of theoretically-obtained chemical shifts based on different geometries.[27] Interestingly, the HOMA values show a larger variability, caused by the differences in the experimental and ab initio optimised geometries. Apart from the numerical values, the tendencies in aromatic character variation as expressed by HOMA and NICS are rather similar.

Analysis of Table 2 leads to a significant finding. In all kinds of systems: (**14**)–(**19**) the aromaticity of both pyrrole and furan fragments depends mostly on the topology of heteroatoms in the system, i.e. on whether there is a [3,2-*b*] or [2,3-*b*] system. The nature of the neighbouring ring is much less important. The mean HOMA and NICS values (at B3LYP/6-311+G**) for the pyrrole ring for [3,2-*b*] and [2,3-*b*] systems are HOMA=0.858, NICS=−15.1 and HOMA=0.776, NICS=−14.1, respectively, which may be compared with the value for the isolated pyrrole calculated at the same level of theory equal to HOMA=0.857 and NICS=−15.0. Practically no change in the aromatic character is observed for the fusion leading to the [3,2-*b*] system contrary to the substantial decrease for the [2,3-*b*] system. Almost the same is observed for furan: the mean value for the first case is HOMA=0.197 and NICS=−11.6, which may be compared with HOMA=0.200 and NICS=−12.2 for the isolated molecule. Again for the [2,3-*b*] systems a substantial decrease in aromaticity is observed: the mean HOMA= 0.060 and NICS=−10.7. It may be concluded that similarly as in the case of benzenoid hydrocarbons,[28] the most important factor which determines the aromatic character of the ring is of a topological nature, i.e. it depends on the position of the heteroatom in the neighbouring fragment rather than on any kind of *endo*-substituent.

Similarly as in the case of thienothiophenes and furofurans[10,11] the aromaticity of furo[2,3-*b*]pyrrole derivatives is remarkably smaller than that of the furo[3,2-*b*]pyrrole ones. Experimental data (for HOMA values) from Table 1 support this clearly. The mean values of HOMA and NICS for the pyrrole fragment in furo[2,3-*b*]pyrrole derivatives are 0.829 and −13.8 ppm, respectively, which can be compared with the relevant values for furo[3,2-*b*]pyrrole isomer: 0.917 and −15.4 ppm. A similar situation is observed in the case of the furan fragment. Consequently, also the mean total value of HOMA (estimated for the whole moiety) for the furo[2,3-*b*]pyrrole system is smaller (mean value of HOMA=0.418) as compared with the [3,2-*b*] structural isomer (mean value of HOMA=0.446). The difference in aromaticity is even more striking when it is based on the optimised geometries at B3LYP/6-311+G** level; for unsubstituted systems the relevant data are 0.349 and 0.483, respectively (see Table 2). The reason for the lower aromatic character of the furo[2,3-*b*]pyrrole isomer is the close structural proximity of the nitrogen and oxygen atoms. This causes a stronger interaction between the heteroatoms leading to much higher alternation of both CO and CN bond lengths. This effect may be explained by the differences between bond lengths: Δ_{CO} for CO and Δ_{CN} for CN bonds. For [2,3-*b*]pyrroles both Δ_{CO} and Δ_{CN} are about three times greater than for the furo[3,2-*b*]pyrrole case.

Additionally, a strong shortening of bond lengths in the O–C–N fragment (of ca. 0.03 Å) as compared with the furo[3,2-*b*]pyrroles system is observed.

The differences in aromaticity follow well the results of recent theoretical analyses on the acidity of the NH proton of the pyrrole fragment[13] and are nicely reflected in the observed stability of both systems. Comparing the course of the Diels–Alder reactions of furo[2,3-*b*]pyrroles with their [3,2-*b*] isomers it was found that the [2,3-*b*]system is a more active diene that its [3,2-*b*] isomer.[29]

Comparison of the aromatic character (expressed both by HOMA and NICS) of substituent species and the parent system reveals that the substituents play a very important role, with electron-accepting groups stabilising the systems. Both total and local aromaticity usually increases significantly in comparison with parent systems e.g. total aromaticity of furo[2,3-*b*]pyrrole increases from HOMA=0.349 up to 0.392–0.451 for systems substituted with formyl- (**9, 10**) or cyano-groups (**11**), basing on B3LYP/6-311+G**. The high variation observed for furo[3,2-*b*]pyrrole system: ΔHOMA (0.385–0.530, based on experimental geometries) is many times greater than any possible error and is significantly larger than that observed e.g. for benzene derivatives.[30] This variation in aromaticity is mostly manifested by changes in bond alternation in the system.[26] The significantly smaller variation of the aromatic character, which is observed in the case of furo[2,3-*b*]pyrrole isomer (ΔHOMA in the range: 0.409–0.440, based on experimental geometries) is most probably due to a small variation of substituent character: only the systems with electron-accepting groups attached in the *2*-position of the furan fragment were stable enough for X-ray diffraction experiment, whereas in the case of furo[3,2-*b*]pyrrole both electron-accepting and electron-donating substituents were present on the furan fragment. According to the Hückel rule,[14] in 4N+2 π-electron systems a decrease (or an increase) of π-electron charge in the system should decrease its aromaticity (and stability). However, it seems that in the case of furo[2,3-*b*]pyrrole and furo[3,2-*b*]pyrrole the substituents not only modify the π-electron structure of the central moiety but may also strongly force the π-electrons localised partly on the heteroatom to be more delocalised over the whole system. Therefore, a strong modification of aromaticity of the formal 4N+2 systems is observed due to substitution, which in turn may strongly affect the reactivity of these systems.[29]

2. Experimental

2.1. X-Ray diffraction

The X-ray measurements of eight crystals of methyl furo[3,2-*b*]pyrrole-5-carboxylate derivatives (4*H* (**1**); 2,3-dimethyl-4*H* (**2**); 2-formyl-4*H* (**3**); 2-(4-chloro-2-methyl)-phenoxy-4-methyl (**4**); 4-benzyl-2-methyl (**5**); 4-benzyl-2,3-dimethyl (**6**); 4-benzyl-2-formyl (**7**); 4-benzyl-2-(4-chloro-2-methyl)phenoxy (**8**)), and of five crystals of methyl furo[2,3-*b*]pyrrole-5-carboxylate derivatives (2-formyl-6*H* (**9**), 2-formyl-6-methyl (**10**), 2-cyano-6-methyl (**11**), 6-benzyl-2-formyl (**12**), 2-cyano-6-benzyl (**13**)), shown in Scheme 1, were made at room temperature on a KM-4 KUMA diffractometer with graphite monochromated CuKα radiation. The data were collected at room temperature using $\omega-2\theta$ scan technique. The intensity of the control reflections varied by less than 5%, and a linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarisation effects, and no absorption correction was applied. The structures were solved by direct methods[31] and refined using SHELXL.[32] The refinement was based on F^2 for all reflections except those with very negative F^2. The weighted *R* factor, *wR* and all goodness-of-fit *S* values are based on F^2. The non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in the calculated positions and their positions and thermal parameters were refined isotropically. The atomic scattering factors were taken from the International Tables.[33] Tables 3 and 4 present the selected crystal data and structure refinement, whereas Tables 5 and 6 present selected bond lengths for compounds (**1**)–(**13**).

Table 3. Selected crystal data and structure refinement for (**1**)–(**8**)

Compound	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)	(**8**)
Empirical formula	$C_8H_7NO_3$	$C_{10}H_{11}NO_3$	$C_9H_7NO_4$	$C_{16}H_{14}ClNO_4$	$C_{16}H_{15}NO_3$	$C_{17}H_{17}NO_3$	$C_{16}H_{13}NO_4$	$C_{22}H_{18}ClNO_4$
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*-1	$P2_1/n$	*P*-1	$P2_1$	*P*-1	*P*-1	$P2_1/n$
Unit cell dimensions:								
a (Å)	17.719 (4)	6.383 (1)	3.808 (1)	6.999 (1)	6.062 (1)	6.767 (1)	9.623 (2)	10.924 (2)
b (Å)	7.785 (2)	7.364 (1)	24.369 (5)	7.842 (2)	9.931 (2)	10.618 (2)	11.091 (2)	9.753 (2)
c (Å)	10.989 (2)	10.668 (2)	9.385 (2)	14.324 (3)	11.462 (2)	11.636 (2)	13.341 (3)	18.030 (4)
α (°)	90	82.69 (3)	90	95.34 (3)	90	63.71 (3)	96.91 (3)	90
β (°)	93.41 (3)	80.20 (3)	100.06 (3)	99.25 (3)	98.64 (3)	83.26 (3)	100.66 (3)	91.44 (3)
γ (°)	90	73.08 (3)	90	102.49 (3)	90	76.38 (3)	96.71 (3)	90
Volume (Å^3)	1513.2 (6)	471.13 (13)	857.5 (3)	750.9 (3)	682.2 (2)	728.4 (2)	1374.9 (5)	1920.3 (7)
Z	8	2	4	2	2	2	4	4
Absorption coefficient (mm^{-1})	0.956	0.845	1.027	2.417	0.743	0.721	0.825	2.004
Reflections collected	1629	2201	1996	3366	1724	3230	6062	4223
Final *R* indices ($I > 4\sigma$)	R=0.0504, wR^2=0.1341	R=0.0418, wR^2=0.1199	R=0.0534, wR^2=0.1446	R=0.0568, wR^2=0.1574	R=0.0353, wR^2=0.0959	R=0.0493, wR^2=0.1337	R=0.0430, wR^2=0.1196	R=0.0458, wR^2=0.1222

Table 4. Selected crystal data and the structure refinement for (**9**)–(**13**)

Compound	(**9**)	(**10**)	(**11**)	(**12**)	(**13**)
Empirical formula	$C_9H_7NO_4$	$C_{10}H_9NO_4$	$C_{10}H_8N_2O_3$	$C_{16}H_{13}NO_4$	$C_{16}H_{12}N_2O_3$
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	*P*-1	$P2_1/c$	$P2_1/c$
Unit cell dimentions:					
a (Å)	5.680 (1)	7.289 (1)	7.143 (1)	13.274 (3)	13.263 (3)
b (Å)	7.942 (2)	16.761 (3)	8.540 (2)	9.157 (2)	9.750 (2)
c (Å)	9.530 (2)	8.087 (2)	8.553 (2)	11.378 (2)	11.104 (2)
α (°)	83.14 (3)	90	97.60 (3)	90	90
β (°)	73.38 (3)	104.66 (3)	112.53 (3)	100.75(3)	101.09 (3)
γ (°)	85.90 (3)	90	95.49 (3)	90	90
Volume (Å^3)	408.7 (2)	955.8 (3)	471.5 (2)	1358.7(5)	1409.1 (5)
Z	2	4	2	4	4
Absorption coefficient (mm^{-1})	1.078	0.960	0.917	0.835	0.768
Reflections collected	1823	2162	2111	3016	3226
Final *R* indices [$I > 4\sigma$]	R=0.0391, wR^2=0.1114	R=0.0521, wR^2=0.1468	R=0.0457, wR^2=0.1272	R=0.0419, wR^2=0.1137	R=0.0429, wR^2=0.1250

Table 5. Selected experimental bond lengths with standard deviation (in parentheses) (Å), the computed bond lengths at B3LYP/6-311+G** (in bold), at HF/6-311+G** (in italics) for (**1**)–(**8**). Labelling of bonds according to Scheme 1

	B1	B2	B3	B4	B5	B6	B7	B8	B9
(**1**)	1.384 (2)	1.348 (2)	1.424 (2)	1.355 (2)	1.383 (2)	1.390 (2)	1.389 (2)	1.369 (2)	1.372 (2)
(**1**)	**1.375**	**1.366**	**1.428**	**1.362**	**1.390**	**1.397**	**1.402**	**1.364**	**1.389**
(**1**)	*1.350*	*1.346*	*1.438*	*1.352*	*1.376*	*1.373*	*1.406*	*1.347*	*1.360*
(**2**)	1.397 (2)	1.359 (2)	1.425 (2)	1.360 (2)	1.387 (2)	1.393 (2)	1.395 (2)	1.369 (2)	1.367 (2)
(**2**)	**1.388**	**1.374**	**1.434**	**1.363**	**1.391**	**1.399**	**1.400**	**1.363**	**1.386**
(**2**)	*1.361*	*1.351*	*1.444*	*1.352*	*1.377*	*1.375*	*1.404*	*1.346*	*1.357*
(**3**)	1.385 (2)	1.368 (2)	1.405 (2)	1.356 (2)	1.374 (2)	1.392 (2)	1.387 (2)	1.367 (2)	1.385 (2)
(**3**)	**1.379**	**1.383**	**1.414**	**1.365**	**1.386**	**1.396**	**1.402**	**1.353**	**1.395**
(**3**)	*1.350*	*1.356*	*1.427*	*1.356*	*1.371*	*1.372*	*1.408*	*1.337*	*1.363*
(**4**)	1.382 (2)	1.340 (3)	1.424 (3)	1.354 (2)	1.384 (2)	1.395 (2)	1.385 (3)	1.379 (2)	1.370 (3)
(**5**)	1.384 (3)	1.358 (4)	1.417 (3)	1.365 (3)	1.389 (3)	1.400 (3)	1.391 (3)	1.370 (2)	1.366 (3)
(**6**)	1.392 (2)	1.356 (2)	1.425 (2)	1.360 (2)	1.389 (2)	1.399 (2)	1.379 (2)	1.366 (2)	1.372 (2)
(**7**)	1.387 (2)	1.369 (3)	1.405 (3)	1.361 (2)	1.389 (2)	1.390 (2)	1.381 (3)	1.360 (2)	1.384 (2)
(**7**)[a]	1.384 (2)	1.374 (2)	1.403 (2)	1.363 (2)	1.387 (2)	1.395 (2)	1.383 (2)	1.366 (2)	1.380 (2)
(**8**)	1.384 (2)	1.346 (2)	1.422 (2)	1.364 (2)	1.391 (2)	1.389 (2)	1.388 (2)	1.379 (2)	1.362 (2)

[a] Two independent molecules in the unit cell.

Table 6. Selected experimental bond lengths with standard deviation (in parentheses) (Å0, the computed bond lengths at B3LYP/6-311+G** (in bold), at HF/6-311+G** (in italics) for (**9**)–(**13**). Labelling of bonds according to Scheme 1

	B1	B2	B3	B4	B5	B6	B7	B8	B9
(**9**0	1.405 (2)	1.355 (3)	1.419 (2)	1.422 (2)	1.368 (3)	1.402 (2)	1.333 (2)	1.339 (2)	1.372 (3)
(**9**)	**1.404**	**1.377**	**1.427**	**1.425**	**1.384**	**1.405**	**1.342**	**1.331**	**1.392**
(**9**)	*1.379*	*1.352*	*1.434*	*1.427*	*1.362*	*1.395*	*1.330*	*1.311*	*1.367*
(**10**)	1.406 (2)	1.370 (2)	1.422 (2)	1.420 (2)	1.374 (2)	1.413 (2)	1.335 (2)	1.341 (2)	1.375 (2)
(**10**)	**1.404**	**1.377**	**1.426**	**1.420**	**1.388**	**1.417**	**1.341**	**1.334**	**1.392**
(**10**)	*1.380*	*1.352*	*1.433*	*1.420*	*1.366*	*1.405*	*1.328*	*1.314*	*1.368*
(**11**)	1.398 (2)	1.359 (2)	1.428 (2)	1.416 (2)	1.378 (2)	1.411 (2)	1.331 (2)	1.349 (2)	1.375 (2)
(**11**)	**1.409**	**1.371**	**1.430**	**1.419**	**1.389**	**1.415**	**1.342**	**1.339**	**1.388**
(**11**)	*1.380*	*1.345*	*1.436*	*1.420*	*1.366*	*1.404*	*1.328*	*1.319*	*1.365*
(**12**)	1.405 (2)	1.367 (2)	1.417 (2)	1.410 (2)	1.375 (2)	1.414 (2)	1.337 (2)	1.339 (2)	1.375 (2)
(**13**)	1.401 (2)	1.356 (3)	1.426 (3)	1.407 (3)	1.376 (3)	1.410 (3)	1.334 (3)	1.343 (3)	1.367 (3)

Further details of the crystal structure: list of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry are deposited in the Cambridge Structural Data Centre[19] with deposition numbers: CCDC155591 (**1**), CCDC155592 (**2**), CCDC155593 (**3**), CCDC155594 (**4**), CCDC155595 (**5**), CCDC155596 (**6**), CCDC155597 (**7**), CCDC 155598 (**8**), CCDC156407 (**9**), CCDC156408 (**10**), CCDC156409 (**11**), CCDC156410 (**12**) and CCDC156411 (**13**).

2.2. Syntheses

The syntheses and the properties of compounds (**1**)–(**13**) are described in details in the literature.[15–18] Starting with the furan-type aldehydes (furan-2-carbaldehyde, 5-methylfuran-2-carbaldehyde, 4,5-dimethylfuran-2-carbaldehyde and 5-(4-chloro-2-methylphenoxy)furan-2-carbaldehyde) with methyl azidoacetate in the presence of sodium methoxide were obtained corresponding azido acrylates which, in turn, by thermolysis in boiling toluene led to the corresponding methyl furo[3,2-*b*]pyrrole-5-carboxylates (**1**) and (**2**).[15] *N*-Methyl and *N*-benzyl derivatives (**4**), (**5**), (**6**) and (**8**) were prepared[16] at the phase-transfer catalysis while the 2-formylated products (**3**) and (**7**) were prepared[16,17] by using the Vilsmeier reaction. Starting from furan-3-carbaldehyde methyl furo[2,3-*b*]pyrrole-5-carboxylate[18] was prepared in the same way as the case of compounds (**1**) and (**2**). The formylated products (**9**), (**10**) and (**12**) were prepared by using the Vilsmeier reaction from methyl furo[2,3-*b*]pyrrole-5-carboxylate and its *N*-Methyl and *N*-benzyl derivatives.[18] 2-Cyano substituted derivatives (**11**) and (**13**) were obtained by reaction of the corresponding 2-formyl derivatives (**10**) and (**12**) with hydroxylammonium chloride in acetic anhydride in the presence of pyridine.

2.3. Computational details

For comparison, the systems (**1**)–(**3**), (**9**)–(**11**) and related compounds have been optimised at ab initio RHF/6-311+G** and DFT B3LYP/6-311+G** levels of theory using the Gaussian94 program.[34] All species corresponded to minima, with no imaginary frequencies. The NICS values[23] for a few systems were calculated at ring centres at GIAO-HF/6-31+G* level of theory using both experimental and computed geometries.

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