The Structures of 2,1,3-Benzoxadiazole (Benzofurazan) and 2,1,3-Benzothiadiazole (Piazthiole) - A Computational Study

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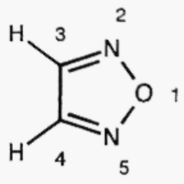
Abstract: The structures of 1,2,5-oxadiazole (furazan, **1**), 2,1,3-benzoxadiazole (benzofurazan, **2**) and 2,1,3-benzothiadiazole (piazthiole, **3**) have been calculated by *ab initio* and density functional theoretical (DFT) methods. Within a given basis a DFT methodology seems to be superior to RHF and MP2 methods.

Although benzofurazanes were already described at the end of the last century[1] the structure of the parent compound (**2**) seems to be unknown[2,4,5]. Certain quantum chemical methods have now reached a state of maturity where reliable results (e.g., bond distances, bond angles) can be obtained with a degree of confidence that they can be judged against experimental data and there are several reports, where experimental data have been scrutinized critically[6]. Therefore a study was undertaken to obtain geometrical data (bond lengths, bond angles) of **2** and **3** which should be more reliable than those reported in[3].



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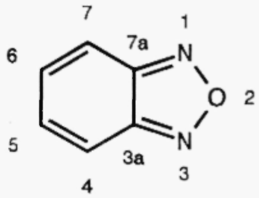

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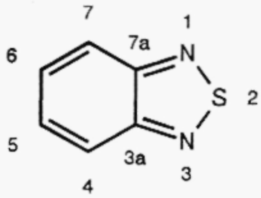

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In order to test the suitability of quantum chemical methods for compounds of this type first calculations were performed for furazan (1,2,5-oxadiazole, **1**)[7], since the exact geometry of this compound has been determined by microwave spectroscopy[8]. In Table 1 the results of semiempirical (AM1, PM3)[9 10], *ab initio*[12-16] and density functional theoretical (DFT) methods[12 17] are given. Obviously DFT methods are most reliable in the prediction of geometrical parameters (bond lengths, bond angles), *but only* if Becke's nonlocal three-parameter exchange and correlation functional[18] in conjunction with the Lee-Yang-Parr correlation functional[19] (B3LYP)[14] are used. These observations are in line with results obtained for other compounds of a similar type (nonclassical furoxans[22], furoxans[23], benzofuroxans[23]).

The extension of these calculations to benzofurazan (**2**, Table 2) reveals that the geometry of the heterocyclic moiety in **2** remains nearly the same as in **1** irrespective the fact that a benzene ring is annulated to **1**. Additionally benzofurazan must be considered as a strongly localized *o*-quinoid system. The stability of these compounds can of course be understood quite simply within the HMO level taking into consideration the principle of topological charge stabilization[24]. Although the exact geometry of **2** seems to be unknown there are a few X-ray data of *substituted* benzofurazans[5]. Compared with these data DFT calculations seem to be most reliable in predicting the geometry of these compounds; the influence of an extended basis set within this methodology (6-31G* → 6-311G**) seems to be only marginal (Table 2).

Table 1: Calculated Data for Furazan (**1**, bond lengths in Å)[a]

Method	ΔH_f°, E	ZPE[d]	$r_{1,2}$	$r_{2,3}$	$r_{3,4}$	ω(1-2-3)	ω(2-3-4)	ω(2-1-5)
AM1	85.49[b]	-	1.334	1.338	1.480	107.43	106.13	112.87
PM3	74.45[b]	-	1.383	1.321	1.453	110.44	106.60	105.91
RHF/6-31G*	-260.54739[c]	31.7	1.333	1.275	1.429	106.51	107.70	111.59
RHF/6-311G**	-260.60846[c]	31.5	1.327	1.273	1.430	106.65	107.52	111.65
MP2/6-31G*	-261.31688[c]	28.8	1.374	1.329	1.404	104.68	109.25	112.16
BLYP/6-31G*	-261.99813[c]	27.5	1.402	1.322	1.431	104.80	109.57	111.32
B3LYP/6-31G*	-262.04701[c]	28.8	1.372	1.307	1.423	105.31	108.90	111.59
B3LYP/6-311G**	-262.11211[c]	28.6	1.369	1.303	1.422	105.44	108.83	111.46
exp.[e]	-	-	1.3729	1.3032	1.4211	105.53	108.89	111.15

[a] All stationary points have been characterized as minima by calculation and diagonalization of the Hessian matrix[20,21]; [b] ΔH_f° in kcal/mol; [c] Energy in a.u.; [d] Zero point vibrational energies (in kcal/mol); [e] See[8a].

Table 2: Calculated Data for Benzofurazan (**2**, bond lengths in Å)[a]

Method	ΔH_f°, E	ZPE	$r_{1,2}$	$r_{1,7a}$	$r_{3a,4}$	$r_{3a,7a}$	$r_{4,5}$	$r_{5,6}$
AM1	113.43	-	1.327	1.352	1.430	1.494	1.361	1.438
PM3	102.99	-	1.374	1.335	1.434	1.456	1.357	1.443
RHF/6-31G*	-413.18139	63.5	1.330	1.285	1.441	1.427	1.340	1.461
RHF/6-311G**	-413.27069	63.0	1.325	1.282	1.440	1.427	1.339	1.462
MP2/6-31G*	-414.45912	-	1.370	1.353	1.414	1.418	1.380	1.427
BLYP/6-31G*	-415.56645	56.2	1.400	1.338	1.432	1.451	1.382	1.445
B3LYP/6-31G*	-415.67801	58.4	1.369	1.323	1.426	1.437	1.368	1.441
B3LYP/6-311G**	-415.77590	56.6	1.365	1.318	1.425	1.436	1.364	1.440
exp.[b]	-	-	1.365-1.377	1.310-1.314	1.423-1.429	1.424	1.340-1.352	1.428

[a] Footnotes as in Table 1; [b] See[5a].

It is of course of interest whether the predictive power of these methods is also applicable to heterocyclic systems which contain second-row elements. 2,1,3-Benzothiadiazole (piazthiole, **3**) was chosen as a model system. The results of various theoretical methods are given in Table 3. Again there seems to exist no exact structure determination of the parent compound **3**, but structures of a few substituted derivatives[25] and metal complexes[26] have been reported. Provided that metal complexation does not change the geometry of the parent compound considerably there is again a good correspondence between experimental data and DFT results *except* the bond distance $r_{1,2}$ (N-S) and $r_{3a,7a}$, which both are calculated approximately 0.02 Å to long.

Table 3: Calculated Data for 2,1,3-Benzothiadiazole (Piazthiole) (**3**, bond lengths in Å)[a]

Method	ΔH_f°, E	ZPE	$r_{1,2}$	$r_{1,7a}$	$r_{3a,4}$	$r_{3a,7a}$	$r_{4,5}$	$r_{5,6}$
AM1	76.02	-	1.636	1.337	1.435	1.495	1.361	1.431
PM3	53.32	-	1.715	1.334	1.437	1.461	1.356	1.438
RHF/6-31G*	-735.91309	60.9	1.620	1.301	1.439	1.441	1.343	1.451
RHF/6-311G**	-736.00367	60.9	1.616	1.300	1.439	1.441	1.341	1.452
MP2/6-31G*	-737.13517	61.5	1.634	1.368	1.413	1.434	1.381	1.421
BLYP/6-31G*	-738.58879	54.9	1.673	1.355	1.432	1.466	1.384	1.439
B3LYP/6-31G*	-738.71690	56.9	1.645	1.339	1.426	1.452	1.371	1.434
B3LYP/6-311G**	-738.82193	56.6	1.640	1.337	1.423	1.449	1.367	1.432
exp.[b]	-	-	1.610-1.628	1.332-1.358	1.407-1.424	1.416-1.428	1.340-1.371	1.411-1.428

[a] Footnotes as in Table 1; [b] See[26].

As already observed for **1** (and **2**) there is no crucial influence of the basis set (6-31G* → 6-311G**). In conclusion it can be stated that DFT methods of the type described above (B3LYP/6-31G*) are valuable theoretical tools for structure determinations of even unusual heterocyclic systems.

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