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Nonclassical Furoxans - A Computational Study

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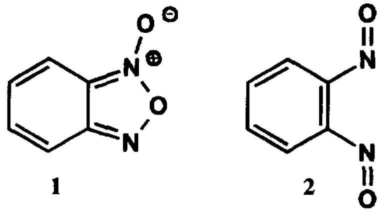
Dedicated to Prof. Dr. Hans Suschitzky on the occasion of his 80th birthday

Abstract: *Ab initio* and density functional theoretical studies on nonclassical furoxans (**4a-c**; **9**, **10**; **15**, **16**; **21a**, **b**; **23**, **24**) and some of their open-chain *o*-dinitroso isomers (**5a-c**; **6a-c**; **7a-c**; **11-14**; **17-20**; **22a**, **b**; **25**, **26**) are presented.

INTRODUCTION

Benzofuroxans (e.g., **1**)[1,2,3] constitute a unique class of molecules in so far as these compounds (as well as furoxans themselves and heteroannulated derivatives) are far more stable than their open-chain 1,2-dinitroso isomers (e.g., **2**)[4], but it is well known that compounds of this type may isomerize quite rapidly obviously involving the *o*-dinitroso arene as an intermediate[1]. Whereas these isomerisations have been investigated rather intensively the detection of **2** was reported only recently[6], but as early as 1975 H. Suschitzky and coworkers described experimental results which could be explained as trapping of an *o*-dinitrosobenzene[7,8,9]. As has been shown [11-16] this phenomenon could be understood theoretically, if quantum chemical *ab initio* methods are used, but the inclusion of electron correlation[17] is mandatory.



1 **2**

method	1[a]	2[b]
RHF/6-31G*	0	-14.7
MP2/6-31G*//6-31G*	0	+10.9
DFT[c]	0	+19.0

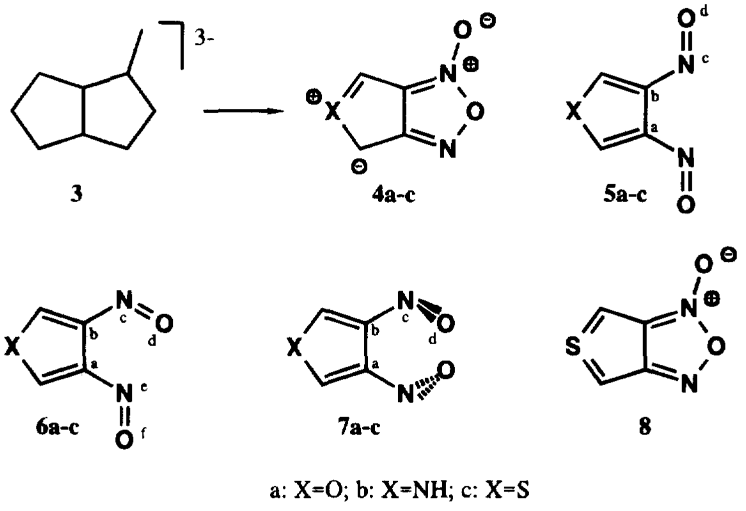
[a] Relative energies in kcal/mol. [b] Minus sign: *more* stable than **1**.
[c] BLYP/6-31G*.

Scheme 1.

In recent years density functional methods (DFT)[18,19] are being used more and more for several reasons. One of the major advantages of these methods lies in the inclusion of electron correlation (comparable with post HF methods at the MP2 level, depending on the precise methodology) together with a remarkable computational speed[20]. As can be seen from the corresponding values of **1** and **2** (Scheme 1) a DFT calculation using Becke's exchange[21] with Lee, Young and Parr correlation functional[22] puts the *o*-dinitroso benzene *above* **1** in agreement with experimental data[2,3] and *ab initio* values at the post HF level[12-15]. Therefore it seemed of interest to extend these calculations to nonclassical furoxans, which have neither been treated by computational methods nor observed (or even trapped) experimentally[23].

RESULTS

Nonclassical[25] furoxans[27] (e.g., **4**) can be formally derived from 1-methylenepentadienyl trianion (**3**) by successive introduction of heteroatoms. Whether such bicyclic structures, which can be depicted as 1,2-dipoles (**4a-c**) or - as in the case of **4c** - with tetravalent sulfur (**8**)[26,29], are minima on the PES (potential energy surface) or are not accessible because their open-chain 3,4-dinitroso isomers (**5a-c**, **6a-c**, **7a-c**) are far more stable is an open question. Our computations on furo[3,4-c][1,2,5]oxadiazole 1-oxide (**4a**), pyrrolo[3,4-c][1,2,5]oxadiazole 1-oxide (**4b**), thieno[3,4-c][1,2,5]oxadiazole 1-oxide (**4c**) and the corresponding *o*-dinitroso compounds (**5a-c**, **6a-c**, **7a-c**) gave the following results.



Scheme 2.

1. Both on the RHF/6-31G* and DFT (BLYP/6-31G*)[30,31] level **4a-c** are minima[32] on the PES (Table1);
2. Both on the RHF and DFT level there are at least three different 3,4-dinitroso conformers (*anti*: **5a-c**; *amphi*: **6a-c**; *syn*: **7a-c**) as minima on the PES (Table 2)[34];

Table 1: Calculated Energies for 4a-c to 7a-c.

Compd.	RHF/6-31G*	ΔE[a,b,c]	MP2/6-31G*//6-31G*	ΔE[a,b,c]	BLYP/6-31G*	ΔE[a,b,c]	ΔE(+ZPE)[a,b,c,d]
4a	-485.80117	0.0	-487.20608	0.0	-488.49858	0.0	0.0
4b	-466.00817	0.0	-467.40688	0.0	-468.64699	0.0	0.0
4c	-808.48538	0.0	-809.84945	0.0	-811.48151	0.0	0.0
5a	-485.89538	-59.1	-487.23772	-19.9	-488.50444	-3.7	-4.6
5b	-466.08995	-51.3	-467.42230	-9.7	-468.65123	-2.7	-4.1
5c	-808.56220	-48.2	-809.85919	-6.1	-811.47999	-1.0	-0.4
6a	-485.89654	-59.8	-487.23836	-20.3	-488.50664	-5.1	-6.0
6b	-466.08964	-51.1	-467.42146	-9.2	-468.65095	-2.5	-3.9
6c	-808.56097	-47.4	-809.85735	-5.0	-811.48196	-0.3	-1.8
7a	-485.89553	-59.2	-487.23749	-19.7	-488.50588	-4.6	-5.4
7b	-466.08723	-49.6	-467.41932	-7.8	-468.64974	-1.7	-3.1
7c	-808.55883	-46.1	-809.85534	-3.7	-811.47661	-3.1	+1.9

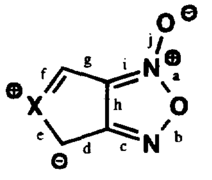
[a] Relative energies. [b] Values in kcal/mol. [c] Minus: *more* stable than 4. [d] ZPE: Zero point vibrational energy (RHF/6-31G* values).

Table 2: Selected Torsion Angles for **5a-c**, **6a-c** and **7a-c**[a]

Compd.	method[b]	ω (a-b-c-d)	ω (b-a-e-f)	Compd.	method	ω (a-b-c-d)	ω (b-a-e-f)
5a	6-31G*	180.0	-	**7a**	6-31G*	6.4	-
	DFT	180.0	-		DFT	0.0[c]	-
5b	6-31G*	180.0	-	**7b**	6-31G*	5.1	-
	DFT	180.0	-		DFT	0.0[d]	-
5c	6-31G*	179.9	-	**7c**	6-31G*	18.9	-
	DFT	179.9	-		DFT	10.3	-
6a	6-31G*	0.0	179.8				
	DFT	7.0	-157.8				
6b	6-31G*	0.0	180.0				
	DFT	0.0	180.0				
6c	6-31G*	0.0	179.9				
	DFT	10.6	-151.7				

[a] Calculated without symmetry restrictions. [b] 6-31G*: RHF/6-31G*; DFT: BLYP/6-31G*. [c] r (O-O) = 2.916 Å. [d] r (O-O) = 2.902 Å.

3. On the RHF level the open-chain isomers (5-7) are far more stable than the nonclassical furoxans (4). The energy difference (ΔE (open - cyclic)) amounts to -46 to -60 kcal/mol, with a significant decrease ($\Delta\Delta E$ = 12-13 kcal/mol) from X=O to X=S (Table 1). As in the furoxan series[11-15] ΔE (open - cyclic) drops sharply when electron correlation is included (Table 1). Based on these data it would not be unexpected if (probably after introduction of substituents which are known to exert a stabilizing influence in other nonclassical systems with two fused five-membered heterocyclic rings[26]) nonclassical furoxans could be either prepared as stable compounds or trapped with suitable agents.



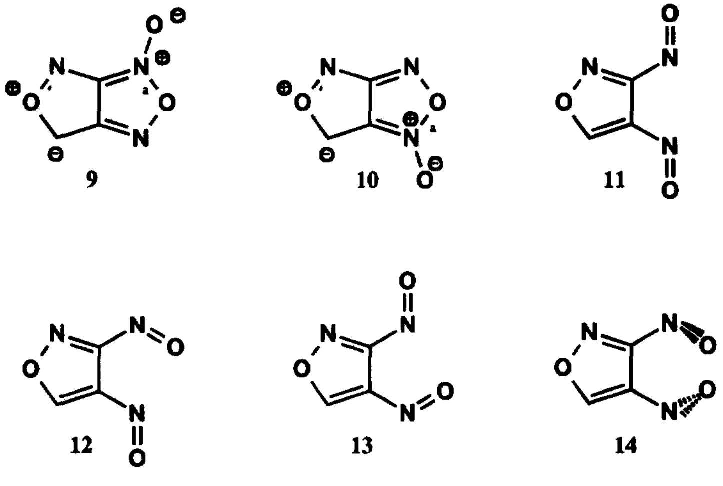
Scheme 3.

Table 3: Calculated Bond Lengths (in Å) for 4a-c

Compd.	method	a	b	c	d	e	f	g	h	i	j
4a	6-31G*	1.283	1.439	1.334	1.369	1.372	1.295	1.371	1.416	1.349	1.191
	DFT	1.623	1.357	1.351	1.403	1.372	1.372	1.395	1.453	1.352	1.231
4b	6-31G*	1.310	1.390	1.314	1.397	1.368	1.328	1.400	1.417	1.320	1.210
	DFT	1.629	1.361	1.346	1.417	1.382	1.383	1.410	1.453	1.345	1.234
4c	6-31G*	1.297	1.398	1.319	1.393	1.695	1.667	1.384	1.420	1.338	1.202
	DFT	1.593	1.364	1.352	1.409	1.730	1.732	1.399	1.453	1.356	1.236

4. As in the case of benzofuroxan (and other annulated derivatives) the geometric data (bond lengths etc.) seem to be in general agreement with expectation with *one major exception*: The endocyclic N-O bond (a in Scheme 3, Table 3) seems to be too short (RHF/6-31G*) or far too long (DFT), although experimental values are of course still lacking[35];
5. All data reported so far are the result of gas phase calculations. The computational introduction of a solvent (presence of acetonitrile (ε = 35.9) using the Onsager model; SCRF option in GAUSSIAN92) does not alter ΔE (open - cyclic) significantly (ΔE_ε (open - cyclic) = E_ε (6a) - E_ε (4a) = -20.4 kcal/mol [MP2/6-31G*// 6-31G*]).

The theoretical treatment of nonclassical furoxans has also been extended to isoxazolo[3,4-c][1,2,5]oxadiazole 3- (1-) oxide (9, 10) and their 3,4-dinitroso compounds (11-14) (Scheme 4).



Scheme 4.

Table 4: Calculated Energies for 9-14

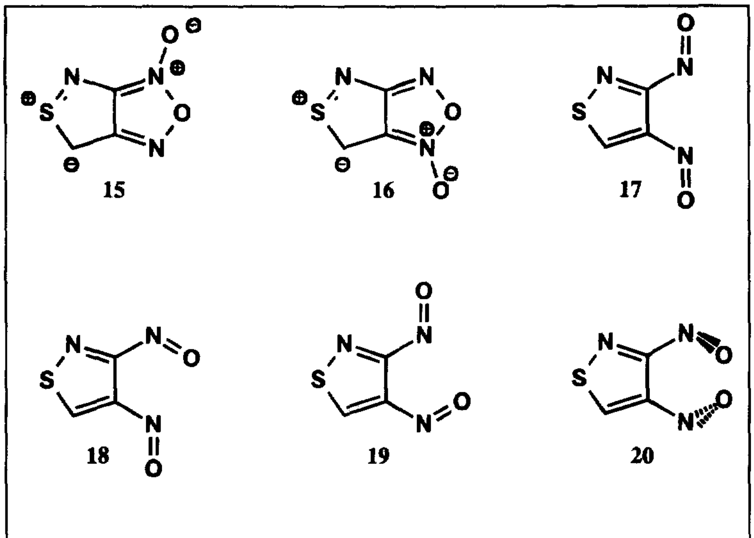
method[a]	9	10	11	12	13	14
6-31G*	-501.74606[b]	-501.76742	-501.84634[d]	-501.84940	-501.84748	-501.84789
ΔE	+13.4[c]	0.0	-49.5	-51.4	-50.2	-50.5
MP2	-503.21537	-503.18939	-503.22518	-503.22756	-503.22567	-503.22608
ΔE	0.0	+16.3	-6.2	-7.6	-6.5	-6.7
DFT	-504.52069	-504.52194	-504.52175[e]	-504.52406	-504.52771	-504.52297
ΔE	+0.8	0.0	+0.1	-1.3	-3.6	-0.7
ZPE	0.05912	0.05896	0.05705	0.05737	0.05753	0.05753
ΔE[f]	+0.9	0.0	-1.1	-2.3	-4.5	-1.5

[a] 6-31G*: RHF/6-31G*; MP2: MP2/6-31G*//6-31G*; DFT: BLYP/6-31G*; ΔE: ΔE (open - cyclic $_{\text{most stable}}$) at each level; ZPE: ZPE (RHF/6-31G*). [b] Energies in a.u. [c] Energy differences in kcal/mol. [d] Transition state (NIMAG=1). [e] Minimum.

[f] Zero point vibrational energies (ZPEs) included.

The results, which are presented in Table 4, will only be commented on briefly.

1. Both 9 and 10 are minima on the PES, with a *strong* preference of 9 on the MP2/6-31G*//6-31G* level and a slight preference of 10 on the DFT level;
2. Compared with 4a the introduction of a further nitrogen atom *reduces* the energy difference between the bicyclic nonclassical furoxan and the monocyclic dinitroso valence tautomer (ΔE (open - cyclic)). Although in all cases the bicyclic furoxan (9, 10) is predicted to be *less* stable than the 3,4-dinitroso isoxazoles (11-14) one may expect an equilibrium within the limits of detectability (ΔE(open - cyclic) = E(12) - E(9) = -7.6 kcal/mol (MP2/ 6-31G*//6-31G* + ZPE (RHF/6-31G*)), ΔE(open - cyclic) = E(13) - E(10) = -4.5 kcal/mol (BLYP/ 6-31G* + ZPE (RHF/6-31G*))).
3. As for 4a-c the bond distance a in 9 and 10 seems to be out of the range of expectation (10: r (a) =1.629 Å).



Scheme 5.

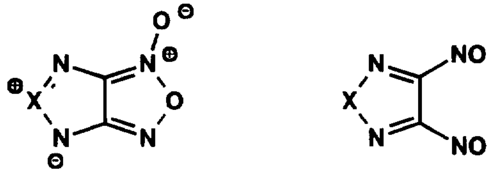
The DFT results for isothiazolo[3,4-c][1,2,5]oxadiazole 3- (1-) oxide (15, 16) and the corresponding dinitroso valence tautomers (17-20) are in general agreement with the data for 9-14. According to these calculations the energy difference between 16 (the most stable furoxan) and 19 (the most stable dinitroso valence tautomer) is calculated to be ΔE (19-16) = +1.4 kcal/mol, i.e., the nonclassical furoxan (16) should be *more stable* than its corresponding dinitroso isomer (19). Whether these values are reliable is of course an open question, but an experimental investigation of this system remains to be a challenge.

Table 5: Calculated Energies for Compounds 15-20 (BLYP/6-31G*)

Compd.	E[a]	ZPE[b]	ΔE[c]
15	-827.52920	29.8	+1.1
16	-827.53113	29.9	0.0
17	-827.52275	28.1	+3.5
18	-827.52397	28.2	+2.8
19	-827.52690	28.7	+1.4
20	-827.51962	28.2	+5.5

[a] Energies in a.u. [b] Zero point vibrational energies in kcal/mol. [c] Relative energies (plus: *less* stable than **16**, ZPEs included).

We have also carried out calculations on [1,2,5]oxadiazolo[3,4-c][1,2,5]oxadiazole 1-oxide (**21a**), [1,2,5]-thiadiazolo[3,4-c][1,2,5]oxadiazole 1-oxide (**21b**) and the corresponding 3,4-dinitroso valence tautomers (**22a,b**).



21a,b **22a,b**

a: X=O; b: X=S

Scheme 6.

Table 6: Calculated Energies of **21a,b** and **22a,b** (in a.u.)

Compd.	method[a]	E[b]	Compd.	method	E
21a	a	-519.12516	**21b**	a	-841.84974
	b	-520.50345		b	-843.54227
22a[c]	a[d]	-519.17077	**22b**[g]	a[e]	-841.85473
	b[e]	-520.50920		b[f]	-843.53415

[a] a: MP2/6-31G*//6-31G*; b: BLYP/6-31G*.

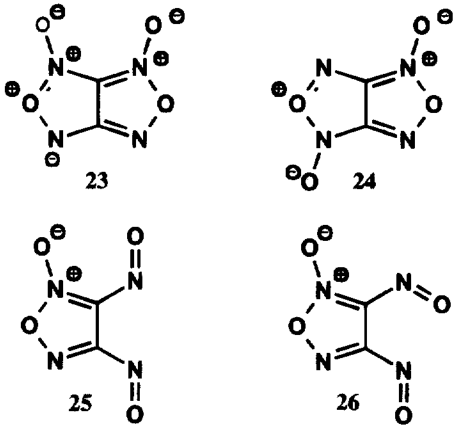
[b] Zero point vibrational energies included (RHF/6-31G* freq and BLYP/6-31G* freq, resp.).

[c] There are at least *three* different minima on the PES (*syn*, *amphi*, *anti*).

[d] *Syn*. [e] *Amphi*. [f] *Anti*. [g] Two different conformers found (*syn*, *anti*).

Some pertinent data are given in Table 6. Again - according to DFT calculations - the bicyclic nonclassical furoxan 21b should be *more stable* than the most stable open-chain valence tautomer (22b, *anti*-3,4-dinitroso[1,2,5]-thiadiazole) by ΔE(22b-21b) = 5.1 kcal/mol (ZPEs included).

[1,2,5]Oxadiazolo[3,4-c][1,2,5]oxadiazole dioxides (furoxano[3,4-c]furoxans; **23**, **24**) are also found as minima on the PES (Table 7). Both MP2/6-31G*//6-31G* as well as DFT calculations put them higher in energy than the corresponding 3,4-dinitroso isomers (four different conformers are found).



Scheme 7.

Table 7: Energies of **23** - **26**[a]

	MP2/6-31G*//6-31G*	BLYP/6-31G*
23	-594.12942	-595.70390
24	-594.17213	-595.70571
25, 26	-594.18643[b]	-595.73689[c]

[a] Values in a.u. [b] **26**; [c] **25** on the PES as minima.

CONCLUSION

As is known from furoxans, benzofuroxans and heteroannulated derivatives the inclusion of electron correlation (MP2 level) is necessary to describe these compounds correctly in comparison with the corresponding *o*-dinitroso valence tautomers. As has been shown in this paper nonclassical furoxans (**4a-c**; **9**, **10**; **15**, **16**; **21a**, **b**; **23**, **24**) are found as minima using *ab initio* (RHF/6-31G*) and DFT (BLYP/6-31G*) methods. As a result of the inclusion of electron correlation (MP2/6-31G*//6-31G*; BLYP/6-31G*) in some cases the energy difference between nonclassical furoxans (**15**, **16**; **22b**) and their *o*-dinitroso counterparts reaches a region where an experimental verification of an equilibrium seems to be possible[37].

ACKNOWLEDGEMENT

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31. Concerning the geometry of thieno[2,3-c][1,2,5]oxadiazole 1- (3-) oxide there are no significant differences between 6-31G* and 6-31+G* (6-311G*, 6-311G**) basis sets. Therefore only the former basis set (6-31G*) has been applied to our calculations.
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34. A *syn* conformer of type 7 with both oxygen atoms on the same side of the molecule seems not to be a minimum on the PES.
35. The same findings were reported for the corresponding bond length in furoxan on the MP2/6-31G*//6-31G* level[11] and is also observed for benzofuroxan (r = 1.604 Å [BLYP/6-31G*]). Preliminary investigations in the [1,2,3]triazole[4,5-c][1,2,5]oxadiazole 4-oxide series indicate, that DFT calculations using Becke's three parameters[36] exchange with Lee, Young and Parr correlation functional (BECKE3LYP/6-31G*)[24] remedy this deficiency of the BLYP functional.
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37. Quite recently an experimental and theoretical study (RHF/6-31G) on the furazan-N-methanide analogue of furoxan and its open-chain isomer (1-nitroso-3-azabutadiene) was published[38]. According to our own calculations the energy difference ΔE is reduced considerably after inclusion of electron correlation (ΔE = 34.1, 11.9, 15.1, 15.1 kcal/mol (RHF/6-31G*, MP2/6-31G*//6-31G*, MP4/6-31G*//6-31G*, BLYP/6-31G*)).
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