

Calculated Structures and Relative Stabilities of Furoxan, Some 1,2-Dinitrosoethylenes and Other Isomers

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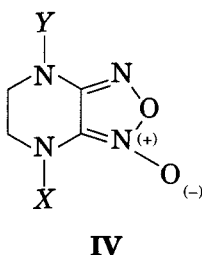
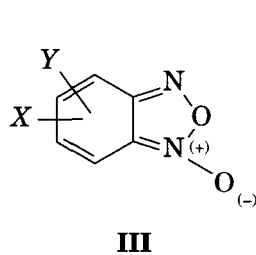
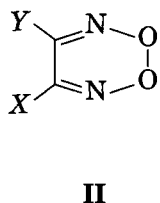
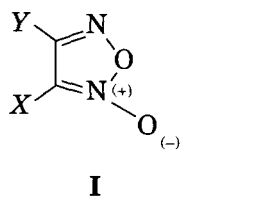
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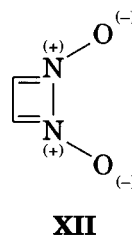
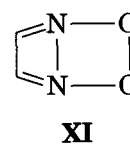
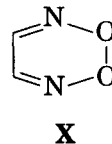
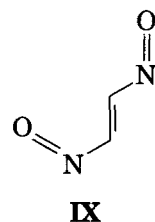
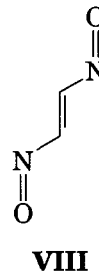
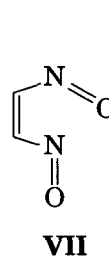
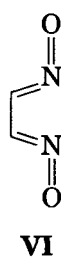
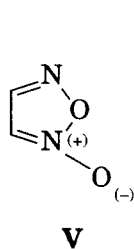
The structures and relative stabilities of furoxan and some of its isomers, e.g., the 1,2-dinitrosoethylenes, have been determined by means of *ab initio* Hartree-Fock and Møller-Plesset calculations. Geometries were optimized at the HF/3-21G, HF/6-31G* and MP2/6-31G* levels, and subsequently used for computing MP2/6-31G*, MP3/6-31G*, and MP4/6-31G* energies. The results are markedly affected by the inclusion of electronic correlation, which renders three of the isomers unstable. It also emphasizes the importance of a zwitterionic contribution to the structure of furoxan, which promotes ring-opening through a *cis* 1,2-dinitrosoethylene intermediate/transition state that has an MP4/6-31G**/MP2/6-31G* energy that is 31.6 kcal/mol above furoxan.

INTRODUCTION

Furoxans (**I**: 1,2,5-oxidiazole-2-oxides) have been known since the mid-19th century,¹⁻⁵ although there was for some time a controversy as to whether their structure was correctly represented by **I** or by the dioxadiazine **II**.⁶ Furoxans with a variety of substituents *X* and *Y* are known, as well as a large group of bicyclic or polycyclic fused systems, e.g., **III** and **IV**.⁶⁻¹¹ Various nitro derivatives of benzofuroxan (e.g., **III**, *X* = *Y* = NO₂) have been investigated as energetic materials.¹²



some furoxan ring-opening reactions proceed through intermediates analogous to these.^{8,13-18}



A number of structural isomeric forms can be drawn for furoxan, **V**. Some of these are shown below (**VI**–**XII**); **VI**–**IX** are conformational isomers of 1,2-dinitrosoethylene. The *cis*-1,2-dinitrosoethylenes **VI** and **VII** are of particular interest, since it is believed that

Ab initio SCF computational studies of **V**–**IX** have recently been carried out, and produced some disagreement concerning the 4-31G and 4-31G* optimized geometries of the *cis*- and *trans*-dinitrosoethylenes.^{19,20} On the basis of one of these studies,¹⁹ it was later suggested that the *cis*-dinitrosoethylene **VI** has a bond between the nitrogens, and should be represented by **XII**.²¹ Support for this idea was pro-

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vided by a topological analysis of the molecule's 6-31G* electron density, using the Bader approach.²²

One of our objectives in this work has been to investigate which of the possible isomers V–XII actually correspond to energy minima, and to determine the relative stabilities of those that do. We shall also examine the ring-opening transition from V to VI/VII.

METHODS

The Gaussian 90 system of programs²³ was used to carry out HF/3-21G, HF/6-31G*, and MP2/6-31G* op-

timizations of V–XII. For each of the Hartree–Fock results and for V and VII at the MP2 level, we verified the existence of a local energy minimum by computing the vibration frequencies and checking for imaginary values. Both the HF/6-31G* and the MP2/6-31G* optimized geometries were used for single-point energy calculations at the MP2/6-31G*, MP3/6-31G*, and MP4/6-31G* levels.

RESULTS AND DISCUSSION

Our calculated structures and energies, presented in Tables I and II, show an unusually marked depend-

Table I. Calculated structures.

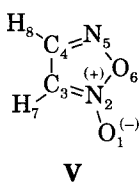
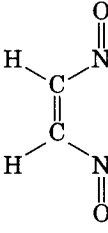
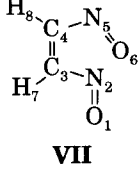
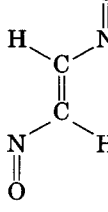
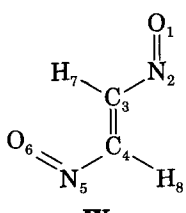
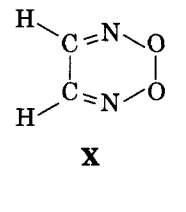
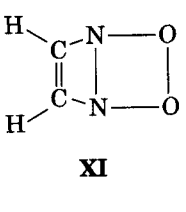
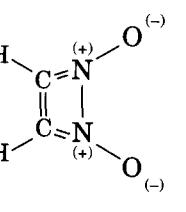
Molecule	Distance (Å) or angle (deg)	HF/3-21G	Method HF/6-31G*	MP2/6-31G*
 V	N ₂ —O ₁	1.289	1.213	1.214
	C ₃ —N ₂	1.295	1.299	1.349
	N ₂ —O ₆	1.430	1.337	1.527
	C ₃ —C ₄	1.424	1.417	1.392
	C ₄ —N ₅	1.284	1.276	1.334
	N ₅ —O ₆	1.442	1.355	1.346
	C—H	1.06	1.07	1.08
	O ₁ —N ₂ —C ₃	133.2	133.1	137.5
	O ₁ —N ₂ —O ₆	118.8	117.9	119.0
	N ₂ —C ₃ —C ₄	107.7	105.0	108.8
	N ₂ —C ₃ —H ₇	122.3	121.5	118.7
	N ₂ —O ₆ —N ₅	106.7	109.5	108.3
	C ₃ —C ₄ —N ₅	112.3	110.4	112.2
	C ₃ —C ₄ —H ₈	126.9	128.6	128.2
	C ₄ —N ₅ —O ₆	105.3	106.1	107.3
	Planar structure			
	N—O	1.222	1.180	1.248
	C—N	1.449	1.433	1.433
	C—C	1.313	1.321	1.347
 VI	C—H	1.071	1.075	1.089
	O—N—C	111.1	112.0	110.5
	N—C—C	121.2	121.1	120.0
	H—C—C	123.0	122.9	123.2
	Planar structure			
	N ₂ —O ₁	1.222	1.180	1.247
	N ₅ —O ₆	1.219	1.176	1.244
	C ₃ —N ₂	1.446	1.428	1.430
 VII	C ₄ —N ₅	1.450	1.438	1.437
	C ₃ —C ₄	1.314	1.320	1.348
	C—H	1.07	1.07	1.09
	C ₃ —N ₂ —O ₁	111.4	112.5	111.2
	N ₂ —C ₃ —C ₄	121.7	121.1	120.2
	N ₂ —C ₃ —H ₇	115.8	116.3	116.9
	C ₃ —C ₄ —N ₅	125.4	125.5	123.2
	N ₅ —C ₄ —H ₈	112.8	112.7	114.1
	C ₄ —N ₅ —O ₆	114.4	114.9	113.3
	O ₁ —N ₂ —C ₃ —C ₄	−174.7	−175.3	−169.1
	C ₃ —C ₄ —N ₅ —O ₆	41.8	52.3	44.5
	N—O	1.222	1.180	1.248
	C—N	1.442	1.428	1.426
	C—C	1.312	1.319	1.345
 VIII	C—H	1.071	1.075	1.089
	O—N—C	112.1	113.0	111.6
	N—C—C	118.3	117.9	117.2
	N—C—H	117.7	117.9	119.0
	Planar structure			

Table I. (continued)

Molecule	Distance (Å) or angle (deg)	HF/3-21G	Method HF/6-31G*	MP2/6-31G*
 IX	N ₂ —O ₁	1.222	1.180	1.248
	N ₅ —O ₆	1.221	1.178	1.244
	C ₃ —N ₂	1.443	1.428	1.425
	C ₄ —N ₅	1.459	1.440	1.444
	C ₃ —C ₄	1.313	1.319	1.345
	C—H	1.07	1.07	1.09
	C ₃ —N ₂ —O ₁	112.0	113.1	111.7
	N ₂ —C ₃ —C ₄	118.0	117.1	116.5
	N ₂ —C ₃ —H ₇	118.0	117.9	119.1
	C ₃ —C ₄ —N ₅	123.5	123.4	122.9
	N ₅ —C ₄ —H ₈	113.9	114.1	114.7
	C ₄ —N ₅ —O ₆	113.8	114.4	112.9
	O ₁ —N ₂ —C ₃ —C ₄	180.0	179.3	178.4
	C ₃ —C ₄ —N ₅ —O ₆	0.1	26.5	26.3
 X	O—O	1.468	1.391	a
	N—O	1.472, 1.473	1.373	a
	C—N	1.260	1.254	a
	C—C	1.466	1.470	a
	C—H	1.069	1.073	a
	N—O—O	109.9	112.0	a
	C—N—O	111.3	112.7	a
	N—C—C	123.3	120.5	a
	C—C—H	119.3	121.8	a
	N—C—C—N	22.0	22.0	a
	N—O—O—N	64.3	64.5	a
 XI	O—O	1.487	1.406	a
	N—O	1.517	1.431	a
	N—N	1.567	1.463	a
	C—N	1.485	1.437, 1.438	a
	C—C	1.319	1.317	a
	C—H	1.062	1.070	a
	N—O—O	91.5	91.1	a
	O—N—N	88.5	88.9	a
	O—N—C	106.0	109.2	a
	C—N—N	85.2	87.1	a
	N—C—C	94.8	92.9	a
	N—C—H	126.5	127.0	a
	C—C—H	138.6	139.9	a
	C—N—N—O	106.2	109.3	a
 XII	N—O	1.245	1.197	a
	C—N	1.287	1.274	a
	N—N	1.727	1.608	a
	C—C	1.494	1.505	a
	C—H	1.062	1.067	a
	O—N—C	143.8	144.3	a
	O—N—N	131.4	128.0	a
	N—C—C	95.2	92.3	a
	N—C—H	128.6	129.0	a
	N—N—C	84.8	87.7	a
Planar structure				

MP2/6-31G optimization did not converge to this structure.

ence upon the level of the computation; they are particularly sensitive to the inclusion of electronic correlation. This may reflect the relative abundance of strongly electronegative heteroatoms and accompanying lone pairs in these systems; the consequences of this should be especially noticeable in V and X–XII, in which these atoms are linked. (Indeed furoxan, V, has been described as “electron-over-

crowded.”²⁴) In such instances, electronic correlation is expected to be especially important.^{25,26}

In the present study, correlation is taken into account in the MP (Møller–Plesset perturbation theory²⁷) calculations. Thus our finding that the attempted MP2/6-31G* optimizations of X–XII fail to converge (Tables I and II) led us to conclude that these systems are not expected to exist, despite the fact that energy

Table II. Calculated relative energies.

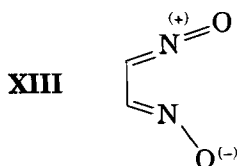
Molecule	Geometry	Energy relative to V, kcal/mol				
		HF/3-21G	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*
 V	3-21G	0	—	—	—	—
	6-31G*	—	0	0	0	0
	MP2/6-31G*	—	—	0	0	0
 VI	3-21G	12.8	—	—	—	—
	6-31G*	—	5.5	32.8	20.5	25.8
	MP2/6-31G*	—	—	34.0	18.2	28.2
 VII	3-21G	16.7	—	—	—	—
	6-31G*	—	9.9	36.3	24.3	29.4
	MP2/6-31G*	—	—	37.3	21.8	31.6
 VIII	3-21G	9.9	—	—	—	—
	6-31G*	—	2.4	29.8	17.5	23.0
	MP2/6-31G*	—	—	31.0	15.1	25.5
 IX	3-21G	12.2	—	—	—	—
	6-31G*	—	6.3	32.8	20.8	25.9
	MP2/6-31G*	—	—	34.1	18.4	28.3
 X	3-21G	6.8	—	—	—	—
	6-31G*	—	32.9	46.7	34.9	40.3
	MP2/6-31G*	—	—	a	a	a
 XI	3-21G	75.8	—	—	—	—
	6-31G*	—	107.4	117.2	104.4	111.7
	MP2/6-31G*	—	—	a	a	a
 XII	3-21G	84.1	—	—	—	—
	6-31G*	—	75.3	48.2	59.6	43.7
	MP2/6-31G*	—	—	a	a	a

MP2/6-31G optimization did not converge to this structure.

minima were confirmed for them at both the HF/3-21G and HF/6-31G* levels. (A similar conclusion was reached some time ago on the basis of bond and strain energy considerations.¹⁴)

In order to gain some insight into why the inclusion of correlation prevents the attainment of equilibrium structures in **X–XII**, we examined the effect of correlation upon the electronic density in **XII**. This system was selected because the topological features of the 6-31G* electronic density in its N—N internuclear region were invoked as indicating the existence of an N—N bond. Accordingly Figure 1 shows the density difference, $\Delta\rho = \rho_{\text{MP2/6-31G}^*} - \rho_{\text{HF/6-31G}^*}$, in the molecular plane of **XII**. (Both densities were computed using the HF/6-31G* optimized geometry.) Correlation is seen to shift electronic density out of all of the internuclear bonding regions and to create charge buildups roughly resembling *p*-orbitals centered at the nitrogen and oxygen nuclei. It is not surprising that these factors work against the formation of a stable molecule.

The effects of electronic correlation are also very striking in the case of furoxan, **V**. There are quite significant differences between the three optimized geometries given for this molecule in Table I, but only the MP2/6-31G* structure shows a marked contrast between the two ring N—O bonds, the N₂—O₆ being much longer and presumably weaker than the N₅—O₆. The HF optimizations predict the ring N—O bonds to be quite similar. While we have been unable to find any experimentally determined structures for furoxan, there are some available for its derivatives.^{28,29} These confirm the tendency for the nitrogen bearing the exocyclic oxygen to have the longer ring N—O bond, although it may be that our data in Table I exaggerate the difference in the two bond lengths. Our MP2/6-31G* structure can be interpreted as indicating a significant contribution from the zwitterion **XIII**, which is certainly consistent with the idea of furoxan ring-opening occurring through *cis*-dinitroso-type intermediates.^{8,13–18*}



For the 1,2-dinitrosoethylenes, **VI–IX**, the three optimization procedures give quite similar results, the major exception to this being that the HF/6-31G* N—O distances are consistently significantly shorter than those predicted by the other two methods. It is notable that all three approaches produce optimized structures, verified as corresponding to energy minima, for both conformations of both the *cis* and *trans* isomers.

*We thank Dr. J. H. Boyer for bringing to our attention the possible importance of **XIII**.

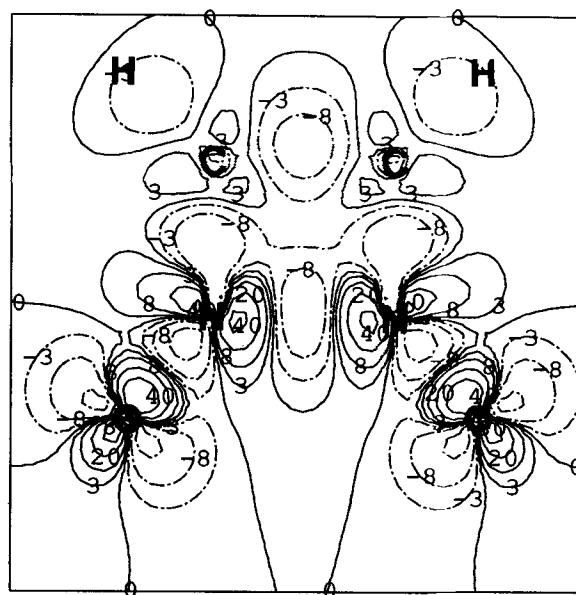


Figure 1. Calculated density difference plot, $\Delta\rho = \rho_{\text{MP2/6-31G}^*} - \rho_{\text{HF/6-31G}^*}$, in the molecular plane of **XII**, in units of 10^{-3} electron/bohr³. Dashed contours correspond to negative density differences.

Electronic correlation is considerably less important in the dinitrosoethylenes than in furoxan. This can be seen in the sharp increases in the energies of **VI–IX** relative to **V** in going from the HF to the MP results (Table II), which reflects the fact that **V** is stabilized much more by the inclusion of correlation than are **VI–IX**.

All of the energy calculations summarized in Table II show **VII** to be the least stable of the four dinitrosoethylenes. **VII** is also expected to be the initial product when furoxan undergoes ring opening, assuming that it is the long N₂—O₆ bond that is broken. In order to achieve a better understanding of furoxan ring-opening, we have sought to find the transition state for the process **V** → **VII**. The N₂—O₆ distance was taken as the reaction coordinate, and the remainder of the structure was optimized for various fixed values of this distance to obtain a potential curve.

At the 3-21G and 6-31G* levels, this procedure produced well-defined transition states, verified to have one imaginary frequency. Their energies were, respectively, 34.0 and 38.0 kcal/mole above **V**, with N₂—O₆ separations of 1.868 Å and 1.829 Å. Once again, however, the inclusion of correlation has important consequences. Instead of a single, clearly defined transition state, the MP2/6-31G* potential curve reaches a plateau, extending over a range of N₂—O₆ distances of at least 0.86 Å and characterized by a number of points satisfying the criterion for a transition state (one imaginary frequency). The local minimum corresponding to **VII**, which has an N₂—O₆ separation of 2.688 Å, can be regarded as a slight indentation in this plateau, having a depth of less

than 0.1 kcal/mol. Indeed, while **VII** does meet the requirement for an energy minimum, of having all real frequencies, one of these is extremely low (50 cm^{-1}), indicating that **VII** is very close to being a transition state.

SUMMARY

This study has shown dramatically the importance of electronic correlation in furoxan and a group of its possible isomers. The inclusion of correlation effects renders three of these unstable, although local energy minima do exist for them at self-consistent-field computational levels. In furoxan, correlation emphasizes the significance of a zwitterionic contribution to the molecular structure, which promotes ring-opening through a *cis*-1,2-dinitrosoethylene intermediate that can be viewed as essentially a transition state.

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References

1. A. Kekulé, *Justus Liebigs Ann. Chem.*, **101**, 200 (1857), **105**, 279 (1858).
2. P. Tönnies, *Ber. Dtsch. Chem. Ges.*, **13**, 1845 (1880).
3. R. Koreff, *Ber. Dtsch. Chem. Ges.*, **19**, 176 (1886).
4. A. Angeli, *Ber. Dtsch. Chem. Ges.*, **26**, 593 (1893).
5. H. Wieland and L. Semper, *Justus Liebigs Ann. Chem.*, **358**, 36 (1907).
6. A. Gasco and A.J. Boulton, *Adv. Heterocycl. Chem.*, **29**, 251 (1981).
7. J.H. Boyer, *Heterocycl. Compd.*, **7**, 462 (1961).
8. J.H. Boyer, *Chem. Rev.*, **80**, 495 (1980).
9. A.R. Katritzky, *Handbook of Heterocyclic Chemistry*, Pergamon Press, New York, 1985, Chapt. 3.4.
10. R.L. Willer and D.W. Moore *J. Org. Chem.*, **50**, 5123 (1985).
11. J.H. Boyer, *Nitroazoles*, VCH Publishers, Deerfield Beach, FL, 1986, Chapt. 5.
12. Y. Oyumi and T.B. Brill, *Combust. Flame*, **65**, 313 (1986).
13. F.B. Mallory, S.L. Manatt, and C.S. Wood, *J. Am. Chem. Soc.*, **87**, 5433 (1965).
14. F.B. Mallory and A. Cammarata, *J. Am. Chem. Soc.*, **88**, 61 (1966).
15. A.R. Katritzky and J.M. Lagowski, *Chemistry of the Heterocyclic N-Oxides*, Academic Press, New York, 1971, pp. 336–338.
16. M.J. Haddadin and C.H. Issidorides, *Heterocycles*, **4**, 767 (1976).
17. J.C. Mason and G. Tennant, *J. Chem. Soc., Chem. Commun.*, 586 (1971).
18. G. Tennant and G.M. Wallace, *J. Chem. Soc., Chem. Commun.*, 267 (1982).
19. E. Sedano, C. Sarasola, J.M. Ugalde, I.X. Irazabalbeitia, and A.G. Guerrero, *J. Phys. Chem.*, **92**, 5094 (1988).
20. S. Marriott, R.D. Topsom, and B.G. Gowenlock, *J. Phys. Chem.*, **94**, 5220 (1990).
21. C. Sarasola, S.C. Choi, J.M. Ugalde, and R.J. Boyd, *J. Phys. Org. Chem.*, **3**, 143 (1990).
22. R.F.W. Bader, *Acc. Chem. Res.*, **18**, 9 (1985).
23. M.J. Frisch, M. Head-Gordon, G.W. Trucks, J.B. Foresman, H.B. Schlegel, K. Raghavachari, M.A. Robb, J.S. Binkley, C. Gonzalez, D.J. Defrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R.L. Martin, L.R. Kahn, J.J.P. Stewart, S. Topiol, and J.A. Pople, Gaussian, Inc., Pittsburgh, PA 1990.
24. M. Calleri, G. Ranghino, P. Ugliengo, and D. Viterbo, *Acta Cryst.*, **B42**, 84 (1986).
25. D.A. Clabo and H.F. Schaefer III, *Int. J. Quantum Chem.*, **31**, 429 (1987).
26. J.M. Coffin and P. Pulay, *J. Phys. Chem.*, **95**, 118 (1991).
27. W.J. Hehre, L. Radom, P.V.R. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley and Sons, New York, 1986.
28. H.L. Ammon and S.K. Bhattacharjee, *Acta Cryst.*, **B38**, 2498 (1982).
29. F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. II*, **S1** (1987).