

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/244269992>

Molecular structure and intramolecular hydrogen bonding in 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone from ab initio molecular orbital calculations

ARTICLE in JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · APRIL 1997

Impact Factor: 1.37 · DOI: 10.1016/S0166-1280(96)04859-2

CITATIONS

8

READS

9

3 AUTHORS, INCLUDING:



Konstantin Borisenko

University of Oxford

83 PUBLICATIONS 1,013 CITATIONS

SEE PROFILE

Molecular structure and intramolecular hydrogen bonding in 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone from ab initio molecular orbital calculations

Konstantin B. Borisenko^{a,b}, Charles W. Bock^{c,d}, István Hargittai^{1,a,b}

^a*Institute of General and Analytical Chemistry, Budapest Technical University, H-1521 Budapest, Hungary*

^b*Structural Chemistry Research Group of the Hungarian Academy of Sciences at Eötvös University, Budapest, Hungary*

^c*Chemistry Department, Philadelphia College of Textiles and Science, Philadelphia, PA 19144, USA*

^d*Institute for Cancer Research, Fox Chase Cancer Center, 7701 Burholme Avenue, Philadelphia, PA 19111, USA*

Received 16 July 1996; accepted 12 September 1996

Abstract

Ab initio molecular orbital calculations using second-order Møller–Plesset (MP2) perturbation theory with the 6-31G* basis set have been performed for 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone. Both molecules are characterized by considerable hydrogen bonding between the nitro and hydroxy groups; pronounced structural changes in other parts of the molecules are observed when compared with the parent phenol and nitrobenzene molecules calculated at the same computational level. These structural changes are consistent with the notion of resonance-assisted hydrogen bonding, also observed in a series of other *o*-nitrophenols and similar molecules. The geometrical and energetic characteristics of the structures indicate somewhat weaker hydrogen bonding in 2,5-dinitrohydroquinone than in 4,6-dinitroresorcinol, which may be interpreted by the difference in the mutual orientation of the substituent pairs in the two compounds. © 1997 Elsevier Science B.V.

Keywords: 2,5-Dinitrohydroquinone; 4,6-Dinitroresorcinol; Intramolecular hydrogen bonding; MP2/6-31G* ab initio calculations

1. Introduction

Recently, we have reported the results of ab initio calculations and electron diffraction structure analyses of a series of *o*-nitrophenols, including 2-nitroresorcinol [1,2], 2-nitrophenol [3] and 4,6-dinitroresorcinol [4]. In all of these molecules, relatively strong intramolecular hydrogen bonding

between the nitro and hydroxy groups was detected, accompanied by pronounced changes in other parts of the molecules when compared with the corresponding structures of phenol [2,5] and nitrobenzene [2,6]. The comparison of the calculated and experimental electron diffraction geometries of 2-nitroresorcinol [2] and 2-nitrophenol [3] was not focused on the absolute values of the structural parameters, but rather on their differences compared with the parent phenol and nitrobenzene molecules. The structural changes derived from electron diffraction studies of 2-nitroresorcinol [2] and 2-nitrophenol [3] were found

¹ For the 1996–1997 academic year, Distinguished Visiting Professor, Department of Chemistry, University of North Carolina at Wilmington, Wilmington, NC 28403, USA.

to be in good agreement with those obtained from ab initio calculations. The structure of 4,6-dinitroresorcinol has previously been determined by gas phase electron diffraction [4], utilizing some constraints from earlier ab initio calculations on 2-nitroresorcinol [2] and 2-nitrophenol [3].

In this work, we continue our investigation of the structural consequences of intramolecular hydrogen bond formation in *o*-nitrophenols. In addition to providing the MP2/6-31G* optimized structure of the previously studied 4,6-dinitroresorcinol [4], we also provide the corresponding information on the molecular structure and intramolecular hydrogen bonding in 2,5-dinitrohydroquinone. For this latter molecule, no route is currently known for its preparation, thus excluding any possibility of an experimental investigation of its molecular structure.

Table 1
4,6-Dinitroresorcinol: computed geometries^a

Parameter	HF/6-31G*	MP2(FC)/6-31G*
C ₁ –C ₆	1.4173	1.4186
C ₅ –C ₆	1.3779	1.3862
C ₁ –C ₂	1.3841	1.3939
C ₂ –H	1.0717	1.0855
C ₅ –H	1.0697	1.0840
C ₅ –C ₆ –C ₁	120.24	120.96
C ₆ –C ₁ –C ₂	118.37	118.01
C ₁ –C ₂ –C ₃	122.10	122.27
C ₄ –C ₅ –C ₆	120.66	119.79
C ₃ –C ₂ –H	118.95	118.87
C ₆ –C ₅ –H	119.67	120.11
C–N	1.4396	1.4546
N–O(⋯H)	1.2075	1.2544
N–O	1.1870	1.2374
C ₁ –C ₆ –N	122.02	121.65
C–N–O(⋯H)	117.80	117.94
C–N–O	118.62	118.80
O–N–O	123.59	123.25
C–O	1.3130	1.3437
O–H	0.9556	0.9873
C ₆ –C ₁ –O	124.66	124.93
C–O–H	110.68	106.98
O⋯H	1.8208	1.7634
O⋯O	2.6049	2.6172
N–O⋯H	107.55	105.92
O–H⋯O	137.29	142.58
Energy (a.u.)	– 787.365408	– 789.553153

^a *r*_c equilibrium bond lengths (Å) and angles (°).

2. Computational details

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 92 series of programs [7]. The standard 6-31G* basis set was used throughout [8]. Initially, RHF/6-31G* optimizations and frequency analyses with the molecules constrained to be planar were made to provide good initial starting geometries for post-Hartree–Fock calculations. These were performed using second-order Møller–Plesset (MP2) perturbation theory [9] to assess the effect of including electron correlation in the calculations, taking advantage of the frozen core option, available in GAUSSIAN series of programs.

3. Results and discussion

The HF/6-31G* and MP2(FC)/6-31G* optimized structural parameters and total molecular energies of 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone are presented in Tables 1 and 2, respectively. The

Table 2
2,5-Dinitrohydroquinone: computed geometries^a

Parameter	HF/6-31G*	MP2(FC)/6-31G*
C ₁ –C ₆	1.3994	1.4167
C ₅ –C ₆	1.3817	1.3931
C ₁ –C ₂	1.3844	1.3947
C ₂ –H	1.0700	1.0844
C ₅ –C ₆ –C ₁	122.19	122.06
C ₆ –C ₁ –C ₂	116.50	116.94
C ₁ –C ₂ –C ₃	121.32	121.00
C ₃ C ₂ H	120.13	120.11
C–N	1.4584	1.4592
N–O(⋯H)	1.2035	1.2539
N–O	1.1848	1.2393
C ₁ –C ₆ –N	121.06	121.06
C–N–O(⋯H)	117.67	117.98
C–N–O	118.33	118.69
O–N–O	123.99	123.33
C–O	1.3308	1.3491
O–H	0.9521	0.9844
C ₆ –C ₁ –O	126.73	126.00
C–O–H	110.62	107.12
O⋯H	1.8554	1.7829
O⋯O	2.6201	2.6249
N–O⋯H	108.51	106.46
O–H⋯O	135.41	141.38
Energy (a.u.)	– 787.3483018	– 789.549150

^a *r*_c equilibrium bond lengths (Å) and angles (°).

Table 3

Parameters of phenol, nitrobenzene and 4,6-dinitroresorcinol from electron diffraction^a and ab initio molecular orbital calculations^b used for comparison

Parameter	Phenol ^c			Nitrobenzene ^d			4,6-Dinitroresorcinol ^e
	HF	MP2	ED	HF	MP2	ED	ED
C _O –C _N	1.385	1.397	1.399(3)	1.383	1.393	1.396(3)	1.424(5)
C–O	1.353	1.375	1.381(4)				1.341(4)
O–H	0.947	0.973	0.958(3)				1.002(9)
∠C–O–H	110.6	108.3	106.4(17)				104.5(14)
∠O–C _O –C _N	122.4	122.8	121.2(12)				123.4(3)
∠C–C _O –C	120.1	120.3	121.6(2)				119.3(3)
N–O(⋯H)							1.241(7)
N–O				1.194	1.242	1.223(3)	1.225(7)
C–N				1.459	1.471	1.486(4)	1.461(4)
∠O–N–O				124.6	124.7	125.3(2)	123.7(2)
∠N–C _N –C _O				117.7	118.6	118.3(3)	121.0(2)
∠C–C _N –C				122.3	122.8	123.4(3)	121.6(3)

^a r_g bond lengths (Å) and r_a angles (°) with estimated total errors parenthesized in the unit of the last digit (ED).

^b r_e equilibrium bond lengths (Å) and angles (°) from HF/6-31G⁺ (HF) and MP2(FC)/6-31G⁺ (MP2) calculations.

^c Ab initio calculations [2]; electron diffraction [5].

^d Ab initio calculations [2]; electron diffraction [6].

^e Ref. [4].

structural parameters of phenol and nitrobenzene from both electron diffraction and ab initio calculations are compiled in Table 3, where the experimental electron diffraction geometry of 4,6-dinitroresorcinol, used for comparison, is also given. The structural changes observed in 4,6-dinitroresorcinol and

2,5-dinitrohydroquinone when compared with the parent compounds, phenol and nitrobenzene, are presented in Tables 4 and 5 respectively.

Generally, including electron correlation in the calculations increases most bond lengths, but decreases the length of the hydrogen bonds; the most

Table 4

Structural changes in 4,6-dinitroresorcinol compared with phenol and nitrobenzene from electron diffraction and ab initio molecular orbital calculations^a

Parameter ^b	Difference: 4,6-dinitroresorcinol/phenol			Difference: 4,6-dinitroresorcinol/nitrobenzene		
	HF	MP2	ED	HF	MP2	ED
C _O –C _N	+ 0.032	+ 0.022	+ 0.025	+ 0.034	+ 0.026	+ 0.028
C–O	– 0.040	– 0.031	– 0.040			
O–H	+ 0.009	+ 0.015	+ 0.042			
∠C–O–H	+ 0.1	– 1.3	– 1.9			
∠O–C _O –C _N	+ 2.3	+ 2.1	+ 2.2			
∠C–C _O –C	– 1.7	– 2.3	– 2.3			
N–O(⋯H)				+ 0.014	+ 0.012	+ 0.018
N–O				– 0.007	– 0.005	+ 0.002
C–N				– 0.019	– 0.016	– 0.025
∠O–N–O				– 1.0	– 1.4	– 1.6
∠N–C _N –C _O				+ 4.3	+ 3.1	+ 2.7
∠C–C _N –C				– 2.1	– 1.8	– 1.8

^a HF/6-31G⁺ (HF) and MP2(FC)/6-31G⁺ (MP2) ab initio calculations.

^b Bond length differences in angstroms, angular differences in degrees.

Table 5

Structural changes in 2,5-dinitrohydroquinone compared with phenol and nitrobenzene from ab initio molecular orbital calculations^a

Parameter ^b	Difference: 2,5-dinitrohydroquinone/phenol		Difference: 2,5-dinitrohydroquinone/nitrobenzene	
	HF	MP2	HF	MP2
C _O –C _N	+ 0.014	+ 0.020	+ 0.016	+ 0.024
C–O	– 0.022	– 0.026		
O–H	+ 0.005	+ 0.011		
∠C–O–H	0.0	– 1.2		
∠O–C _O –C _N	+ 3.6	+ 3.2		
∠C–C _O –C	– 3.6	– 3.4		
N–O(⋯H)			+ 0.010	+ 0.012
N–O			– 0.009	– 0.003
C–N			– 0.001	– 0.012
∠O–N–O			– 0.6	– 1.4
∠N–C _N –C _O			+ 3.4	+ 2.5
∠C–C _N –C			– 0.1	– 0.7

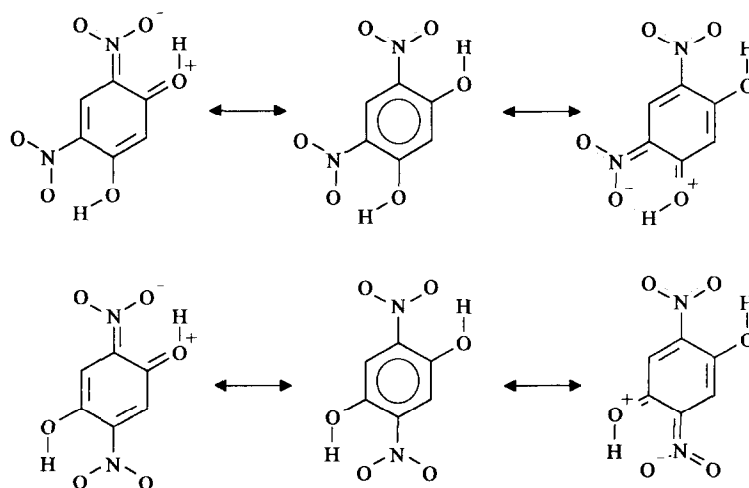
^a HF/6-31G* (HF) and MP2(FC)/6-31G* (MP2) ab initio calculations.^b Bond length differences in angstroms, angular differences in degrees.

pronounced change in the bond angles is a decrease in the C–O–H angle by as much as 4°. The inclusion of electron correlation improves the agreement between the calculated and experimental results (see Table 4). The calculated C–N bond shortening in 2,5-dinitrohydroquinone compared with nitrobenzene appears to be too small at the RHF/6-31G* level (see Table 5).

The geometrical consequences of intramolecular hydrogen bond formation in 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone from the MP2(FC)/6-31G* optimizations are similar to those described

for a series of other ortho-substituted benzenes, i.e. 2-nitroresorcinol [1,2], 2-nitrophenol [3], salicylaldehyde [10] and 2-iminomethyl-phenol [11]. Thus the C–N and C–O bonds decrease and the C–C bond between the substituents, the N–O bond participating in hydrogen bond formation and the O–H bond increase in both molecules compared with the respective bonds in phenol and nitrobenzene. These changes are in good agreement with those suggested by the resonance quinonoid structures shown in Scheme 1.

The structure of 2,5-dinitrohydroquinone shows somewhat smaller changes compared with phenol



Scheme 1.

Table 6

Parameters directly characterizing hydrogen bonding in 2-nitroresorcinol, 4,6-dinitroresorcinol, 2-nitrophenol and 2,5-dinitrohydroquinone from ab initio molecular orbital calculations^a

Parameter	2-Nitroresorcinol ^b	4,6-Dinitroresorcinol	2-Nitrophenol ^c	2,5-Dinitrohydroquinone
O...O	2.585	2.617	2.616	2.625
O...H	1.734	1.763	1.766	1.783
O-H...O	142.4	142.6	142.3	141.4
N-O...H	105.7	105.9	105.9	106.5

^a r , equilibrium bond lengths (Å) and angles (°) from MP2(FC)/6-31G* ab initio calculations.

^b Ref. [2].

^c Ref. [3].

and nitrobenzene than does that of 4,6-dinitroresorcinol (Table 4 and Table 5). Moreover, the increase in the O...O and O...H distances and in the N-O...H angle and the decrease in the O-H...O angle, as shown in Table 6, may point to a somewhat weaker hydrogen bond in 2,5-dinitrohydroquinone than in 4,6-dinitroresorcinol. Shorter O...O and O...H distances are generally associated with stronger hydrogen bonding. It is also generally considered to be more favorable to have larger rather than smaller O-H...O angles, 180° being the ideal arrangement. On the other hand, a stronger hydrogen bond is anticipated to appear with a smaller N-O...H angle, since this will mean greater involvement of the oxygen electron density (with decreasing presence in the close vicinity of the oxygen atom) (meaning, of course, one of the two oxygen lone pairs of electrons which participates in the hydrogen bond). However, the difference may be quite small. To estimate the

hydrogen bond energies in 2,5-dinitrohydroquinone and 4,6-dinitroresorcinol, the conformer in which one of the two hydroxy groups is rotated by 180°, so as to preclude nitro group–hydroxy group interaction, was optimized at the MP2(FC)/6-31G* level. The energy differences between such a conformer and the all-hydrogen-bonded form are 41.4 and 38.9 kJ mol⁻¹ for 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone, respectively. The smaller energy difference for 2,5-dinitrohydroquinone may indicate a weaker hydrogen bond in this molecule than in 4,6-dinitroresorcinol. In both molecules, the two hydrogen bonds are symmetrically positioned; in one case (I) they are related by reflection, and in the other (II) by inversion (Fig. 1).

The difference in the hydrogen bonding of I and II may be attributed to the mutual location of the pairwise interacting nitro and hydroxy groups. It appears that the hydroxy group–nitro group interaction shifts electron density from the hydroxy group towards the nitro group, and this shift is related to intramolecular hydrogen bond formation. In 4,6-dinitroresorcinol,

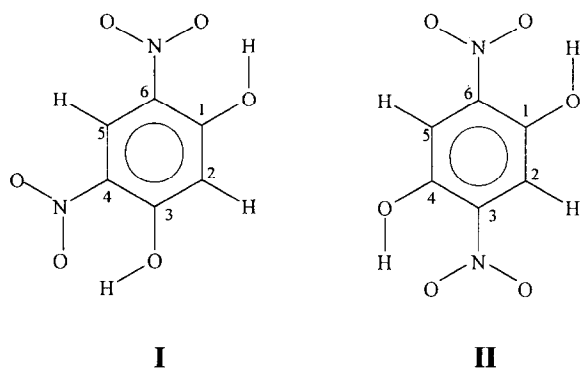
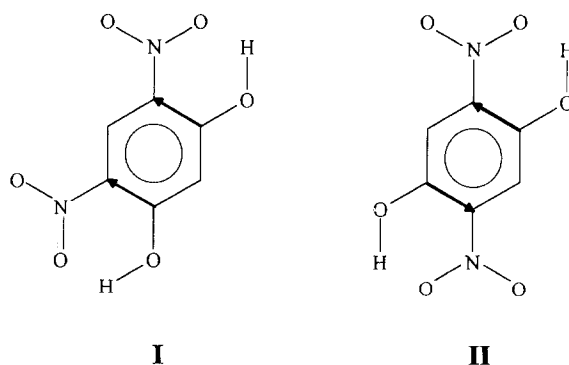


Fig. 1. Molecular models and numbering of atoms in 4,6-dinitroresorcinol (I) and 2,5-dinitrohydroquinone (II). It should be noted that the numbering of the atoms in the model of 2,5-dinitrohydroquinone (II) is the same as that in the model of 4,6-dinitroresorcinol (I) for comparison.



Scheme 2.

the mutual location of the two pairs of interacting groups may increase this shift of electron density, because the directions of the shifts caused by each interacting pair coincide, leading to greater electron redistribution and, consequently, stronger hydrogen bonding. In 2,5-dinitrohydroquinone, the shifts of the electron density, caused by each interacting nitro–hydroxy pair, counteract each other, thus resulting in a smaller overall electron density redistribution and, consequently, weaker intramolecular hydrogen bonding (Scheme 2).

4. Conclusions

There is considerable resonance-assisted intramolecular hydrogen bonding in both 4,6-dinitroresorcinol and 2,5-dinitrohydroquinone. This can be recognized not only in the relatively short O···H and O···O distances, but also in the structural changes in the rest of the molecules when compared with the appropriate parent molecules.

The hydrogen bonding in 2,5-dinitrohydroquinone is somewhat weaker than in 4,6-dinitroresorcinol as witnessed by its longer O···H and O···O distances, smaller hydrogen bond energy and less pronounced geometrical changes in the rest of the molecule. However, similarities, rather than differences, dominate in

the hydrogen bondings of the two molecules, the two hydrogen bonds being related by symmetry in both molecules.

References

- [1] K.B. Borisenko and I. Hargittai, *J. Phys. Chem.*, 97 (1993) 4080.
- [2] C.W. Bock and I. Hargittai, *Struct. Chem.*, 5 (1994) 307.
- [3] K.B. Borisenko, C.W. Bock and I. Hargittai, *J. Phys. Chem.*, 98 (1994) 1442.
- [4] K.B. Borisenko, K. Zauer and I. Hargittai, *J. Phys. Chem.*, 99 (1995) 13 808.
- [5] G. Portalone, G. Schultz, A. Domenicano and I. Hargittai, *Chem. Phys. Lett.*, 197 (1992) 482.
- [6] A. Domenicano, G. Schultz, I. Hargittai, M. Colapietro, G. Portalone, P. George and C.W. Bock, *Struct. Chem.*, 1 (1990) 107.
- [7] A.M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart and J.A. Pople, *GAUSSIAN 92*, Gaussian Inc., Pittsburgh, PA, 1992.
- [8] W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.*, 56 (1972) 2257. P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, 28 (1973) 213.
- [9] C. Møller and M.S. Plesset, *Phys. Rev.*, 46 (1934) 618.
- [10] K.B. Borisenko, C.W. Bock and I. Hargittai, *J. Phys. Chem.*, 100 (1996) 7426.
- [11] K.B. Borisenko and I. Hargittai, *J. Mol. Struct. (Theochem)*, 388 (1996) 107.