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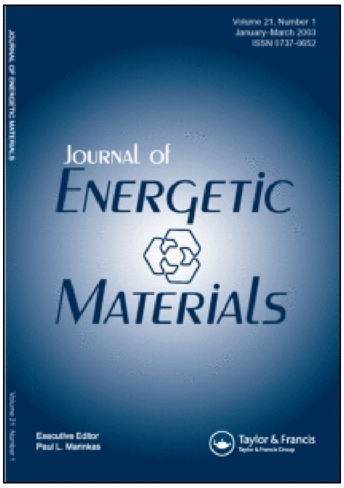

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Resonance-assisted hydrogen bonds in nitrobenzenes

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RESONANCE-ASSISTED HYDROGEN BONDS IN NITROBENZENES §

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ABSTRACT

Based on crystal structural data of 155 substituted nitrobenzenes, geometries of intramolecular hydrogen bonds were examined, which strongly suggested that the hydrogen bonds were enhanced by the resonance which exists in the conjugated system. The atomic partial charges calculated at STO-3G level and other experimental data confirmed also the phenomenon.

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INTRODUCTION

Nitrobenzene and its derivatives are a class of compounds, important in industry, chemistry and biology. They are also important military and commercial explosives. This class of compounds could be divided into two subclasses according to whether or not there is alpha C-H linkage. They behave quite differently in impact experiment and thermal decomposition [1]. The subclass with no alpha C-H linkage consists of mostly nitroanilines

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and nitrophenols, some of which are well known thermal stable explosives (e.g. 1,3,5-triamino-2,4,6-trinitrobenzene ,TATB). The difference in their properties must be originated from their structures, particularly molecular structures. In this respect, intramolecular hydrogen bonding is an important factor to be considered. Reported in this communication is the detailed study on intramolecular hydrogen bonding geometries, ab initio atomic partial charges and acidity of the invovled H atoms in this class of compounds. The device of Resonance-Assisted Hydrogen Bond (RAHB), developed by Gilli and co-workers [2,3] to study the covalent nature of strong homonuclear hydrogen bond in a system of π-conjugated double bonds, was employed and the characteristics could well be rationized in this class of compounds in which the intramolecular hydrogen bonds are either homonuclear (O—H···O) or heteronuclear (N–H··O) and the π - conjugated system is based on a benzene ring.

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THE DATABASE

A search for nitrobenzene crystal structures was done on the CSD [4] (1991 release) with the following criteria. In the structure there should be: 1). only one benzene ring and no other ring; 2). at least one nitro group directly attached to the benzene ring; 3). no other element than C, H, N, O, F, Cl, Br, I. Besides, the structure must be fully determined and disorder-free. Structures containing complicated substitutent or COOH group were excluded so that attention could be focused on the function of the nitro group. The database thus obtained consists of 155 structures in which there are a total of 289 nitro groups [5].

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Table 1. Intramolecular Hydrogen Bonding in Nitrobenzenes

No.	Refcodes	Group[a]					d1	δ2	δ3	δ4	R	δe	τ
		2	3	4	5	6	(A)	(A)	(A)	(A)		(e)	(°)
1	ONITAN	NH2					1.371	-.060		.007	2.666	.027	2.2
							1.350	.023		.025	2.630		3.7
2	QQQFNG02	NH2			NO2		1.352	.019	.039	.025	2.621	.045	4.3
3	CUZDEG	NH2	NO2				1.339	.037		.012	2.609	.034	8.1
								.051		.007	2.620	.030	5.3
4	TNIOAN	NH2	NO2		NO2		1.340	.057	-.006	.001	2.626	.037	8.7
								.053	.006	.028	2.616	.036	22.5
5	TNITAN	NH2	NO2		NO2	NO2	1.312	.073	-.021	-.001	2.717		44.5
								.061	-.015	-.008	2.621		2.4
6	DATNBZ	NH2	NO2		NO2	NH2	1.323				2.520	.008	3.7
										.058	2.585	.056	5.0
							1.317				2.518	.048	3.7
										.048	2.602		6.0
7	BEWYOR	NH2	NO2	NH2	NO2	F	1.315	.063		.001	2.591	.047	17.2
											2.516		5.5
							1.319	.043	.013		2.608		22.7
											2.509		5.5
8	TATNBZ	NH2	NO2	NH2	NO2	NH2	1.309				2.493		3.3
											2.484		3.4
							1.319				2.507		3.3
											2.480		0.7
							1.311				2.502		3.4
											2.492		0.7
9	BAKLII	NH2	NO2	NH2	NO2	OH	1.313				2.535		15.5
											2.751		54.8
							1.320				2.586		8.9
											2.504		15.5
10	FMANIL	V	NO2		CF3		1.322	.076	.021	.025	2.606		5.1
							1.339	.054	.032	.021	2.622		6.1
11	MBDNAN	V	NO2		Br	CH3	1.320	.013	.051	-.012	2.607		5.9
12	MNIAAN01	K			CH3		1.397	.018		-.008	2.662		12.3
							1.399	.020		-.012	2.657		18.0
13	MNIAAN02	K			CH3		1.400	.008		.009	2.635		7.6
14	MNIAAN10	K			CH3		1.410	-.001		-.022	2.918		44.4
15	CUNTOU	X2					1.363	.007		.002	2.622		0.0
16	CUNVAI	X2			NO2		1.369	.055	-.009	.015	2.635		3.0
17	DIXDUJ	X3					1.395	.005		.011	2.657		19.0
18	BDNFAN	X1	NO2		CF3		1.327	-.004	.018	-.056	2.574		4.3
19	JAKJOU	X4	NO2		NO2		1.331	.068	.020	.013	2.644		11.6
							1.335	.046	.020	.013	2.601		1.2
20	KEJGIP	X5	NO2		NO2		1.410	.014	.005	.009	2.777		38.5
21	NPHDZB	X6			NO2		1.329	.045	.035	.010	2.610		2.8
22	ONITPH	OH					1.339	.010		.030	2.590	.066	2.4
23	DNPHOL	OH	NO2				1.337	.007	.016	.027	2.557	.069	3.5
24	DNOPHL	OH			NO2		1.331	.008	.017	.032	2.594		2.2
25	DNOPHL01	OH			NO2		1.343	.021	.035	.016	2.609	.060	2.6
26	KECRUF	OH			CH3		1.354	.021		.051	2.559	.073	3.5
27	NTCPOL	OH			Cl		1.329	.009		.046	2.610		0.8
28	NTCPOL01	OH			Cl		1.342	.024		.041	2.587	.072	0.8

29	CDNPOL	OH	Cl		NO_2		1.333	.036	.008	.037	2.558	.074	5.1
30	BDNPOL	OH	Br		NO_2		1.333	.012	.027	.013	2.599		9.4
31	PICRAC	OH	NO_2		NO_2		1.312	.005	.022	.026	2.553	.067	7.3
							1.358	.002	.015	.030	2.555		1.9
32	PICRAC11	OH	NO_2		NO_2		1.309	.024	.013	.015	2.580		8.9
							1.369	.024	.000	.041	2.537		2.7
33	BAKLI1	OH	NO_2	NH_2	NO_2	NH_2	1.332	.041	.053	.036	2.486		8.9
34	BOCNEM	OH	NO_2		NO_2	OH	1.326	.032	.011	.018	2.593		
							1.326	.032	.011	.018	2.593		
35	BAFLEZ	CH_3	NO_2	Cl			1.501	.012	.001	-.018	2.808	-.008	58.2
36	CMNBEN10	CH_3	NO_2	Cl	CH_3		1.523	.074	-.018	.012	2.807	.004	86.0
37	DOHCOS	CH_3	NO_2	CH_3	NO_2	T	1.502				3.052		84.3
							1.518				3.027		77.8
38	DOHCOS10	CH_3	NO_2	CH_3	NO_2	T	1.502				3.052		84.3
							1.518				3.027		77.8
39	DOHCUY	CH_3	CH_3	CH_3	NO_2	T	1.512	.015		-.009	3.050		79.9
40	DOHCUY10	CH_3	CH_3	CH_3	NO_2	T	1.510	-.002		.006	3.031		79.9
41	FULYEQ10	CH_3	CH_3	CH_3	CH_3	NO_2	1.516	-.023		.000	2.981		57.9
							1.507	-.020		-.016	2.971		58.3
42	NIBZAL	CHO					1.490	.005		-.006	2.701	.001	27.6
43	TNOXYL	CH_3	NO_2	CH_3	NO_2		1.495	.010	-.005	.000	2.834		75.2
							1.495	.010	-.005	.000	2.834		72.0
44	ZZZMUC01	CH_3	NO_2		NO_2		1.505	.036	-.006	-.035	2.849	-.000	51.8
								.026	-.053	-.004	2.925	-.012	60.1
45	NOMESL	CH_3		CH_3		CH_3							66.5
46	SAZHAC	CH_3	NO_2	CH_3	CH_3	CH_3							90.0
47	PMNTBZ	CH_3	CH_3	CH_3	CH_3	CH_3							86.1

a: Symbols in column Groups lists substitute groups in the positions 2 to 6 with short notation: X_1 NH-C(CH_3)$_3$, X_2 NH-N=C(CH_3)$COCH_3$, X_3 $NHCOCH_3$, X_4 NH-NH_2, X_5 NH-$COOC_2H_5$, X_6 NH-N=CH-C_2H_5, K $NHCOCH_3$, T C(CH_3)$_3$, V $NHCH_3$ and blank for H atom. In position 1 there is always a NO_2.

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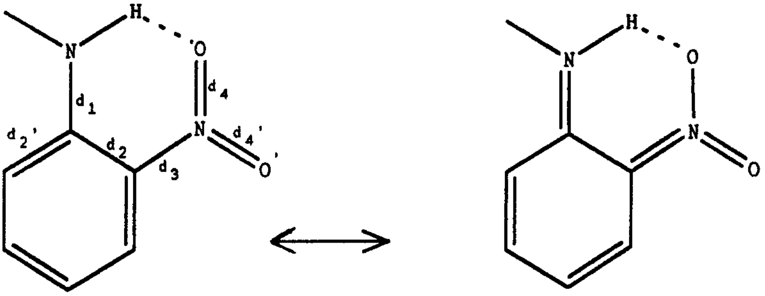

(I)

(II)

Fig. 1 Resonance-Assisted Hydrogen Bond in Nitrobenzenes

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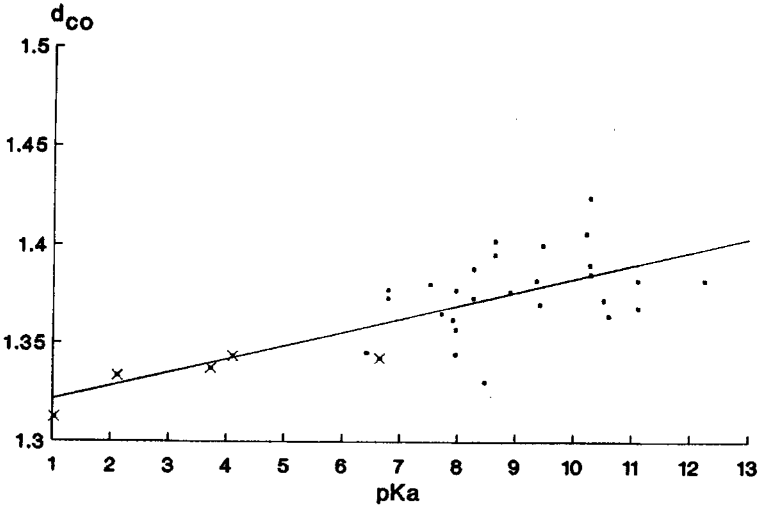

Fig. 2 A scatter plot of pKa versus d_{CO} in ortho-substituted phenols (x: nitrophenols)

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RESULTS AND DISCUSSION

In a total of 155 structures, there are 34 structures in which at least a hydrogen-bond donor group such as NH_2 or NHR (subclass 1) and OH (subclass 2), is directly attached to the benzene ring and ortho- positioned to a nitro group. Intramolecular hydrogen bond was found in all the structures with no exception. There are also 25 structures in which there is a hydrogen-bond donor group but not directly attached to the benzene ring (subclass 3) and 13 structures in which a CH_3 group is directly attached to the benzene ring and ortho- positioned to the nitro group (subclass 4).

For subclass 3, possible intramolecular hydrogen bonding geometry was also examined and intramolecular hydrogen bonds were found in these structures, but not listed in table 1 because no resonance was found. For subclass 4, an attempt was made to search the weak intramolecular hydrogen bond between C SP^3 - H and O in nitro group [6], but none was found. In subclass 4, the nitro group makes a large dihedral angle (in table 1) with benzene ring, showing no sign of forming a system of π–conjugated double bonds. The average value is 68.4°, that is, the plane of NO_2 group is more or less perpendicular to the best plane of benzene ring [7]. Instead, one of the hydrogen atoms in CH_3 is approximately equidistantly positioned to two oxygen atoms in NO_2 group.

The main results were listed in table 1. The column Group listed substituents in position 2 to 6. In position 1 there is always a NO_2 group. For the meanings of the symbols in table 1, see fig.1. d_1 is the bond length between the donor group and its attached ring carbon atom involved in intramolecular hydrogen bonding. Donor group could be OH or NH_2 or NHR or CH_3. R is the contact distance between the two electronegative atoms involved. The τ is the dihedral angle between the best planes of benzene ring and NO_2 group involved in intramolecular hydrogen bonding. All the other columns listed the differences: d2 = d2 - d2' ; d3 = d3' - d3 and d4 = d4 - d4'. The unprimed and primed values respectively are the bond lengths involved and not-involved in hydrogen bonding in the same molecule. If the comparison is not possible, there is a blank in the table.

In subclasses 1 and 2, the ring formed by atoms involved in intramolecular hydrogen bond is almost coplanar with the benzene ring plane in all structures. The maximum deviation from the best plane of the benzene ring for a non-hydrogen atom is 0.10 Å, as shown also by the values of τ in table 1. The R value of 2.48 to 2.65 in structures Nos. 1 to 34 suggested that the hydrogen bonds were strong or even very strong.

After a close look at the bond lengths involved in intramolecular hydrogen bond in subclasses 1 and 2, an inherent trend was found. The bond lengths d_1 and d_3 (fig. 1) are shorter with almost no exception when compared with those corresponding values which are not involved in intramolecular hydrogen bonding in the same molecule. On the other hand, the d_2 and d_4 (fig.1) are longer than those corresponding values. The differences are not very large, but still statistically significant.

The regular shortening and lengthening of the bonds could be rationalized if one considers the resonance between the structures I and II shown in fig.1, where donor group could be NH_2 or NHR or OH. The resonance was first suggested by Gilli and co-workers [2,3] to explain the strong and very strong hydrogen bonds in a system of π-conjugated double bonds. It was concluded

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that while the O···O distance is shortened, the hydrogen bond is transformed from a dissymmetrical O—H··· O electrostatic interaction to a covalent and symmetrical O—H··· O bond and that such behavior is common to all homonuclear hydrogen bonds, while heteronuclear ones can only give weaker bonds of mostly electrostatic nature. In this study, the system of π- conjugated double bonds is based on aromatic benzene ring, not a π-conjugated double bonds, and hydrogen bonds are either homonuclear (O—H·····O) or heteronuclear (N—H·····O), and hydrogen bonds studied are limited to intramolecular ones. Despite these differences, the hydrogen bonds are similiar to the so-called Resonance-Assisted Hydrogen Bond (RAHB) indicated by the following facts: (1) the atoms involved in the hydrogen bond are basically coplanar. (2) the distance O....O is shortened from 2.80 Å to the range of 2.48 to 2.65 Å. (3) the shortening and lengthening of the bonds involved are consistent with the resonance. (4) Nitroanilines and nitrophenols are much more stable than other nitrobenzenes where no such a resonance exists.

The data for subclass 4 (Nos.35 - 46) were also listed in table 1 for comparison reason. As shown by the table, subclass 4 is completely differenet from subclasses 1 and 2. There is no resonance at all. It is consistent with the well known fact in explosives practice, that is, nitrobenzenes with a C--H linkage in the position alpha to the nitro group are significantly different from nitroanilines and nitrophenols used in explosive industry [1]. The latter is considerably more stable than the former because considerably extra stability is gained if one considers the above resonance.

To verify further this hypothesis, atomic charges at STO-3G level were

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calculated with Gaussian-82 program [8] for structures studied within the limitation for our computing facility. The molecular geometries used in the calculation were directly taken from crystal structural data with hydrogen atoms being placed and the bond lengths involving H atoms being chosen according to standard geometry [9]. No geometry optimation was performed. The δe in table 1 is the PC(O) -- PC(O'), PCs being the atomic partial charges for oxygen O and O', respectively (fig.1). The resonance not only lengthens the bond (d_4), but also makes the oxygen atom O charged more negatively . The differences are impressive.

If the resonance makes the d_1 shorter(fig.1), the H atom should be more acidic. In fig. 2, the relation between the d_1 and the pKa was plotted for ortho-substituted phenols, pKa being the minus logarithm of dissociation constant as an acid. Nitrophenols form strong intramolecular hydrogen bonds because they meet the conditions for the resonance. Other phenols, ortho-substituted by group such as halogen atom or alkyl group, does not meet the conditions. The clustering in fig.2 confirms also that the resonance does enhance the hydrogen bonds.

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REFCODES FOR 155 NITROBENZENS

BAFLEZ
BENCLN02
BENCLN03
BICNUW
BRNIBZ
CAGPUV
CLNIBZ
CLNIBZ01
CLNOBE01
CLNOBE02
CMNBEN10
CMBZHM
DAPHUX
DCTNBZ
DEFDUN
DEFDUN01
DEJWEU
DEJWIY
DNBENZ10
DNITBZ
DNITBZ11
DOHCOS
DOHCOOS1
DOHCUY
DOHCUY10
DOXWIW
DUXSIY
ENPROP
FABHOF
FALPEN
FAMDEC
FOFCIM
FUDGOA
FULYEQ10
GACGAS
GASDOT
HNOBEN
ITNOBE
JAZKOK
JAZLAX
KAYSUY
KESNEB
MBZHIC
NACPON10
NIBZAL
NIBZAL01
NIPHAZ
NITBAL01
NITBAL10
NITOLU
NITRBE
NMBZAX
NOMESL
NPBUDO
NPCBNZ
NPIVHB
PCLNBZ
PMNTBZ
PNBZNT
QQQECG01
SAPYEN
SAWBIB
SAZHAC
SEMTAF
SEYGUY
TNBENZ10
TNOXYL
VACBAC
VEGBEO
VEGBIS
ZZZFYW01
ZZZMUC01
ACNPHY
BDNFAN
BERPAP
BEWYOR
BICXIU
BOWSIP
CITYOT10
CLONAN
CUNTOU
CUNVAI
CUZDEG
DATNBZ
DCNDMA
DIMNAN
DIXDUJ
DNIALN
ENPCOY
FADNAN
FANTBZ
FAWWIJ
FBATNB
FENOAN
FMANIL
FNDMAN
FOCVOI
FUGTIK
FUGTIK01
FUXNAN
JAPKIU
JARLOD
KAYTUZ
KEJGIP
MBDNAN
MENPND10
MNIAAN
MNIAAN01
MNIAAN02
MNIAAN10
MNIANL10
MNOMAN10
MNTDMA
MTNANL
MTNOAN10
NANILI
NPHDZA
NPHDZB
NPHYAC
ONITAN
PNTCAN
QQQFNG02
SECMOC
SEJNEA
TATNBZ
TNIOAN
TNITAN
VUYKUV
AMNPHA
BAKLII
BDNPOL
BOCNIQ
BOCPIS
BUBLOZ
BURKUU
CDNPOL
DEMSOD
DNOPHL
DNOPHL01
DNPHOL
FESNEW
FESNIA
FUDZIN
KECRUF
MNPHOL
MNPHOL02
MNPHOL10
NITPOL
NTCPOL
NTCPOL01
ONITPH
PICRAC
PICRAC11
PNIANS
TNPHNT

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