Ab initio calculations of the electron density in the molecules of substituted 1-(4-fluorophenyl)-3-phenyltriazenes

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The tautomeric conversion in substituted 1-(4-fluorophenyl)-3-phenyltriazenes

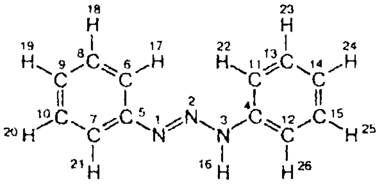
$$\underset{\textbf{A}}{4\text{-}FC_6H_4NHN{=}NC_6H_4X} \rightleftharpoons \underset{\textbf{B}}{4\text{-}FC_6H_4N{=}NHNC_6H_4X}$$

depends on the nature of the substituent X and is determined by the equilibrium constant $K_T = [B]/[A]$. It was demonstrated[1] that electron-withdrawing substituents shift the equilibrium to form **B**, while electron-donating substituents favor an increase in the content of tautomer **A**. However, according to the theory of prototropic tautomerism,[2] the equilibrium should be shifted to the form that exhibits lower acidity. Based on general considerations, one would expect that the substituent will affect the electron density on the nearest nitrogen atom or, to put it differently, the acidity of form **B**, to a greater extent. However, according to the data in Table 1 (see Ref. 1), the electron-donating substituent (4-MeO) destabilizes form **B** by shifting the equilibrium to tautomer **A**. On the contrary, the presence of the electron-withdrawing substituent (3-F) favors the formation of form **B**. It can be suggested that this behavior is associated with the fact that the substituent has a more substantial effect on the acidity of form **A** and, correspondingly, on the electron density on the amine nitrogen atom of this form.

Table 1. Experimental constants of the tautomeric equilibrium (K_T),[1] the values of q and the differences (Δq) between the electron densities on the amine N atom in tautomeric forms **A** and **B**, and the differences between the total energies (ΔE_{tot}) of the tautomeric forms of 1-(4-fluorophenyl)-3-phenyltriazenes for a number of substituents in one of the aromatic ring

X	K_T	q(**A**)	q(**B**)	Δq	ΔE_{tot} /kcal mol^{-1}
4-NH_2		7.7963	7.7930	0.0033	1.7570
4-MeO	0.48	7.7948	7.7937	0.0011	0.5644
4-H	1.8	7.7936	7.7926	0.0010	−0.8780
4-Me	2.4	7.7945	7.7939	0.0006	−0.3763
4-F	1.0	7.7930	7.7930	0	0
4-Cl	1.8	7.7921	7.7923	−0.0002	−0.7535
3,5-Cl_2	3.1	7.7904	7.7954	−0.0050	−1.1303
3-F		7.7920	7.7982	−0.0062	−1.3805
4-NO_2	11.8	7.7886	7.7972	−0.0086	−2.5117

To test this suggestion, we calculated the electron density on the N atoms in 1,3-diphenyltriazene molecules containing substituents in one of the aromatic rings. The structure of 1,3-diphenyltriazene was calculated by the Hartree—Fock method with the 6-31G* basis set and with full geometry optimization using the GAUSSIAN-90 program.[3] The results of calculations are given in Table 2. The atomic numbering scheme is shown below.



All atoms of the molecule are in a single plane (to within 0.002 Å). The interatomic distances and the bond angles in the phenyl rings differ only slightly from the corresponding mean values.

We carried out all subsequent studies with the use of the calculated geometries of the compounds because the results of X-ray diffraction study of 1,3-diphenyltriazene[4,5] depend substantially on the packing factors. We assumed that the substituents X in the benzene ring affect only slightly the geometry of the nucleus. This allowed us to model substituted 1,3-diphenyltriazenes under consideration by the straightforward insertion of a substituent into the phenyl ring. The geometry and the position of the substituent with respect to the ring were preliminarily calculated for molecules of substituted benzenes. Table 1 gives the differences between the total energies of the tautomeric forms and the differences in the electron density on the amine N atom in forms **A** and **B**, which were calculated by the Hartree—Fock method with the 6-311G basis set for a number of substituents using the GAMESS program.[6] It is readily seen that the substituents have a more substantial effect on the electron density on the remote nitrogen atom, while these substituents often have the opposite effect on the nearest nitrogen atom. Thus, the electron-with-

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Table 2. Bond lengths (*d*) and bond angles (ω) in the 1,3-diphenyltriazene molecule calculated by quantum-chemical methods and determined experimentally (X-ray diffraction data)

Bond	*d*/Å			Angle	ω/deg		
	Calculations	Experiment			Calculations	Experiment	
		Data of Ref. 4	Data of Ref. 5			Data of Ref. 4	Data of Ref. 5
N(1)—N(2)	1.221	1.27	1.27	N(1)—N(2)—N(3)	113.5	116	115
N(2)—N(3)	1.323	1.31	1.32	N(2)—N(3)—C(4)	122.5	116	120
N(3)—C(4)	1.392	1.38	1.41	N(2)—N(1)—C(5)	115.5	119.7	114.5
N(1)—C(5)	1.418	1.40	1.43	N(1)—C(5)—C(6)	124.9	125	124.5
N(3)—H(16)	0.999	—	—	N(3)—C(4)—C(11)	122.3	122.5	121
C(5,4)—C	1.391	1.39	1.37	N(2)—N(3)—H(16)	116.6	—	—
C—C(aver.)	1.385	1.375	1.373	C—C—C(aver.)	120.0	120	120
C—H(aver.)	1.075	—	—	C—C—H(aver.)	120.0	—	—

drawing substituent 4-NO_2 increases the electron density on the nearest nitrogen atom. A good correlation is observed between the logarithm of the constant of the tautomeric equilibrium and the difference in the total energy of two tautomeric forms. The correlation equation takes the following form:

$$\log K_T = -0.4281 E_{tot} - 0.0059, \ s = 0.1207, \ r = -0.9668.$$

To summarize, *ab initio* calculations demonstrated that the introduction of a substituent into the Ph ring of 1-(4-fluorophenyl)-3-phenyltriazene affects more substantially the electron density on the remote nitrogen atom, which is, apparently, associated with the high degree of electron conjugation in the triazene system. The correlations obtained allow one to predict the position of the tautomeric equilibrium for a wide range of substituents based on quantum-chemical calculations.

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