

Bonding in 1,2,3-Triazoles VII. Effects of *N*-Substitution. *Ab Initio* Calculations on Model Systems

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Ab initio LCAO-MO-SCF calculations have been performed for the triazole anion, 1*H*- and 2*H*-triazole, and the 1,2- and 1,3-triazolium ions (double-zeta basis set, polarization functions). The geometry of the triazole skeleton was determined by energy minimization of the triazole anion with a double-zeta basis set of lower accuracy. The resulting geometry is partly verified via geometrical correlations obtained from the crystal structures of several 1,2,3-triazoles. The deformation densities for the different types of substitution show a high degree of additivity that is also present in several parameters obtained by Mulliken population analyses. Similar additivity rules also apply to several orbital energies, including the energies of the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO).

Previously a set of correlations have been established for the endocyclic angles of the class of 1,2,3-triazoles, where the *N*-substituted atoms are either carbon or hydrogen.¹ It is concluded that only the position of the *N*-substituents have a significant effect on the geometry of the triazole ring. Two models were analyzed. The first model establishes an approximate linear relationship between the endocyclic angle at a nitrogen atom and the sum of the endocyclic angles at its neighbours. In the second model the sum of the endocyclic angles at the carbon atoms was analyzed as a function of the position of the *N*-substituents. This angular sum is, irrespective of differences in the *C*-substituents, constant for each type of *N*-substitution. Both models have qualitatively been related to changes in hybridization due to substitution, and the present study is an attempt to explain or to find counterparts in the electronic structures of the different types of substituted compounds. The analysis is performed along the following lines: The geometry of the triazole anion is optimized, and the resulting geometry is used as the skeleton for the substituted compounds. There are two reasons for using this approach. It makes it possible to compare electron densities, and the number of parameters influencing the analyses is kept at a minimum.

Computational details

The calculations are of *ab initio* LCAO-MO-SCF type using the Hartree–Fock–Roothaan formalism.² The basis functions are of the contracted Gaussian type. For the

optimization of the geometry of the triazole anion primitive sets of the form (X/7,3), X = C, N³ and (H/3)⁴ were applied in the contractions <X/4,2> and <H/2>, respectively. The exponents for H were scaled by (1.24)². The notation (X/s, p, d) indicates the number of primitive cartesian Gaussians of s-, p- and d-type on atom X. The optimization was performed by minimizing the total energy via the SIMPLEX method,⁵ with C–H distances of 1.07 Å and H–C–C angles of 125°.

On the basis of this geometry *ab initio* LCAO-MO-SCF type calculations with larger basis sets were carried out on the triazole anion, 1*H*- and 2*H*-triazole and the 1,2- and 1,3-triazolium ions. The compounds are henceforth referred to as T0, T1, T2, T12 and T13, respectively.

In these calculations primitive sets of the form (X/9,5,1) and (H/4,1) were used in the contractions <X/4,2,1> and <H/2,1>. The basis functions of s- and p-type for C and N and of s-type for H are from Ref. 3. However, the exponents for hydrogen have been scaled by a factor of 1.3. Polarization functions of d-type for C and N and of p-type for H have been used with exponents of 0.63, 0.95 and 0.8,⁶ respectively. The joint MOLECULE–ALCHEMY program system^{7,8} was used for the calculations.

Results and discussion

Geometry of the triazolate ion. The endocyclic angles of the optimized triazole anion (Table 1) may be tested by the correlations described in Ref. 1. The expected value for the angle at the carbon atoms is 108.35(17)°, and the deviation, 0.22°, is 1.3 times the estimated standard deviation.

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Table 1. The optimized geometry of the triazole anion.^a

Atom	Coordinates/Å		Atoms	Distance ^b /Å	Atoms	Angle ^b /°
	y	z				
N1	-1.1113	1.2762	N1-N2	1.357(1.334)	N1-N2-N3	109.96(113.0)
N2	0.0	2.0549	N1-C5	1.343(1.359)	N2-N3-C4	106.89(105.4)
C4	0.6933	0.0	C4-C5	1.387(1.384)	N3-C4-C5	108.13(108.1)

^aThe numbering of the triazole skeleton is shown in Fig. 1. The molecule has C_{2v} symmetry, $x=0$ for all atoms. ^bValues in parentheses are average values observed in the benzotriazole anion.

tion on the expectation value. From the angles at N1 and N3 an angle of 109.8° is estimated for N2. Thus, the values of the endocyclic angles are in good agreement with the correlations detected in Ref. 1.

The geometry may also be compared to the crystal structure of tetramethylammonium benzotriazolide⁹ (Table 1). The largest deviation is found for the endocyclic angle at N2. However, it has been found that if the C-substituents together with the triazole ring form a condensed ring system, the angle at N2 increases. With the differences in C-substituents in mind, it may be concluded that the optimized geometry of the triazole anion is in reasonable agreement with experiment.

Difference densities. Contour maps of the electron differences have been computed for the four substituted triazoles relative to the anion. The in-plane difference densities show a high degree of delocalization in contrast to the difference densities in the π -region (Figs. 2a-d), which show an accumulation of charge at the substitution sites. For all types of substitution an accumulation of charge is observed along the C-H bonds. Along the bonds in the ring, changes in the electron density at one end of the bond are compensated for by changes of opposite sign at the other end. This pattern of behaviour is similar to the pattern observed for the changes in the endocyclic angles in benzotriazole compounds, changes that have been related to changes in hybridization.

A high degree of additivity is observed in the density changes. This is shown in Figs. 3a-c for the σ - and π -regions. The difference between T12 and T2 results in a map very similar to the difference density for T1. The difference between these two maps, i.e. $T12 - T2 - (T1 - T0)$,

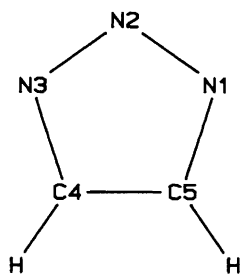


Fig. 1. The geometry of the triazole anion with atomic labelling.

is depicted in Fig. 3d. The numerically highest contours ($0.008 e a_0^{-3}$) are located around the atomic centers, whereas the major parts of the maps have densities numerically less than $0.002 e a_0^{-3}$. This indicates the high degree of accuracy of the additivity.

Population analyses and additivity. The results of the Mulliken population analysis¹⁰ on gross atomic charges and overlap populations are given in Table 2. Supplementary results used in the discussion are listed in Table 3. As expected, the negative atomic charges decrease on substitution. The general trends in the overlap populations are in fair agreement with the trends in the distribution of the distances observed in 1,2,3-triazoles. One exception is constituted by the N-N bond in T0, which seems too large compared to the value of the overlap population. As is also observed for the experimental C-C distances, the C-C overlap populations group into two categories, one consisting of T0, T1 and T13, which are not 2-substituted, and the other consisting of the 2-substituted compounds T2 and T12, with a somewhat longer C-C distance.

The numbers given in Tables 2 and 3 exhibit some degree of additivity. The examinations of additivity have been performed by means of the two models summarized in Tables 4 and 5. The models assume linearity in the substitution effects. In model 1 the quantities in question are symmetric with respect to the two-fold axis of the triazoles skeleton. In model 2 the asymmetry due to asymmetry in the substitution pattern is taken into account.

Table 6 lists the results obtained by model 1 analyses of the C-C overlap populations and of the sum of the charges at the carbon atoms. Similar results are obtained for the π - and σ -parts of the overlap populations, the sum of σ - and s -electrons at the carbon atoms and with less accuracy the sum of π -electrons (r.m.s. = 0.03). Thus model 1 gives a good description of the average electronic properties at the carbon atoms.

Analyses of the charges at the nitrogen atoms give much poorer results. This may be due to the more or less arbitrary way in which charge is partitioned. The good results for the carbon atoms are probably due to the averaging of adjacent atoms.

Model 2 analyses of charges failed for both carbon and nitrogen atoms, whereas analyses of the C-N and N-N overlap populations give reasonably good results (r.m.s. = 0.022 and 0.020). Very good agreement is,

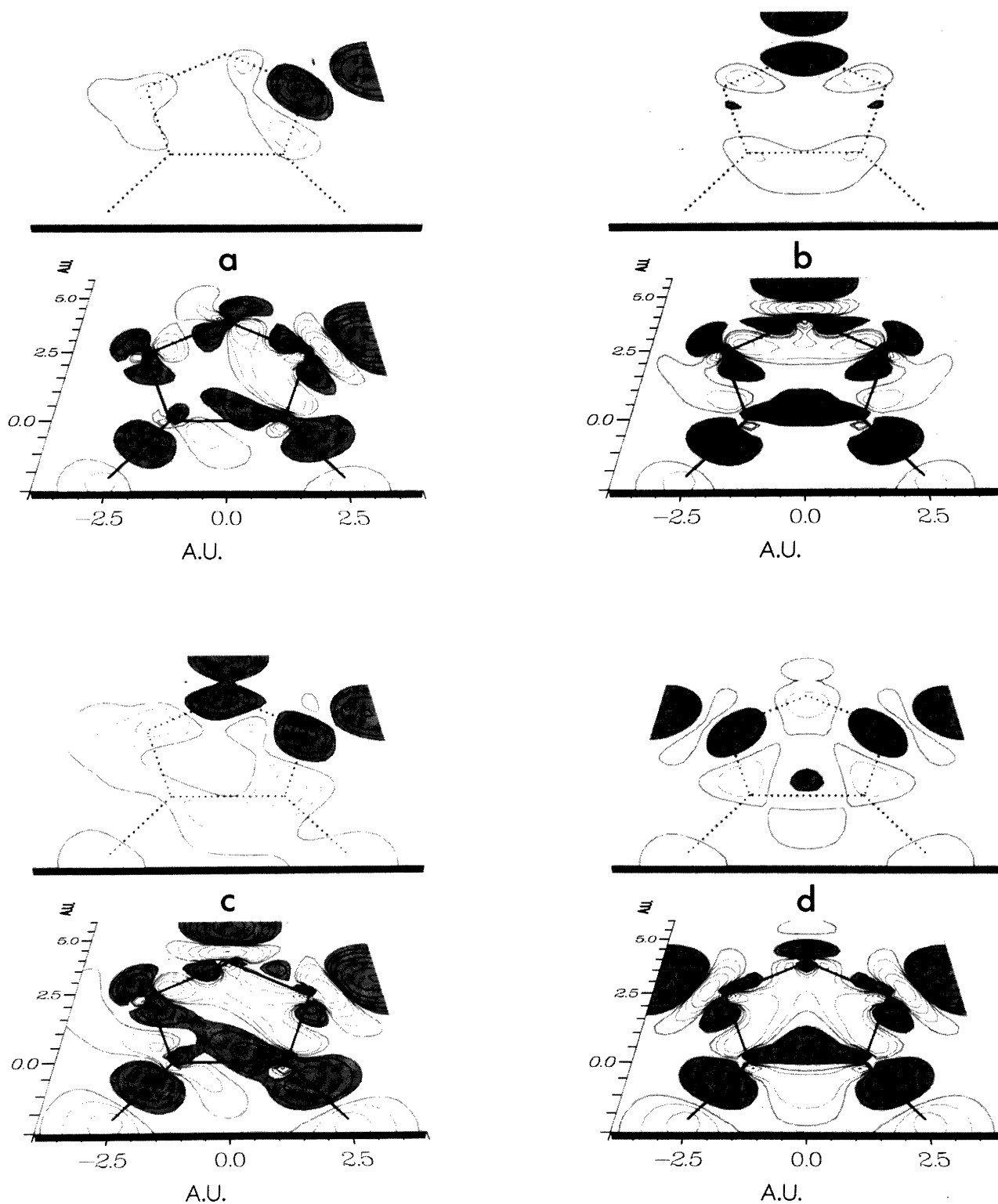


Fig. 2. Difference densities of T1 (a), T2 (b), T12 (c) and T13 (d) relative to T0. The bottom plane is the in-plane difference density, and the top plane is the difference density in the π -region, $1 a_0$ above the molecular plane. Dark areas indicate accumulation of electronic charge, bright areas indicate drain of electrons. First contours are $\pm 0.002 e a_0^{-3}$. Neighbouring contours differ by a factor of 2.

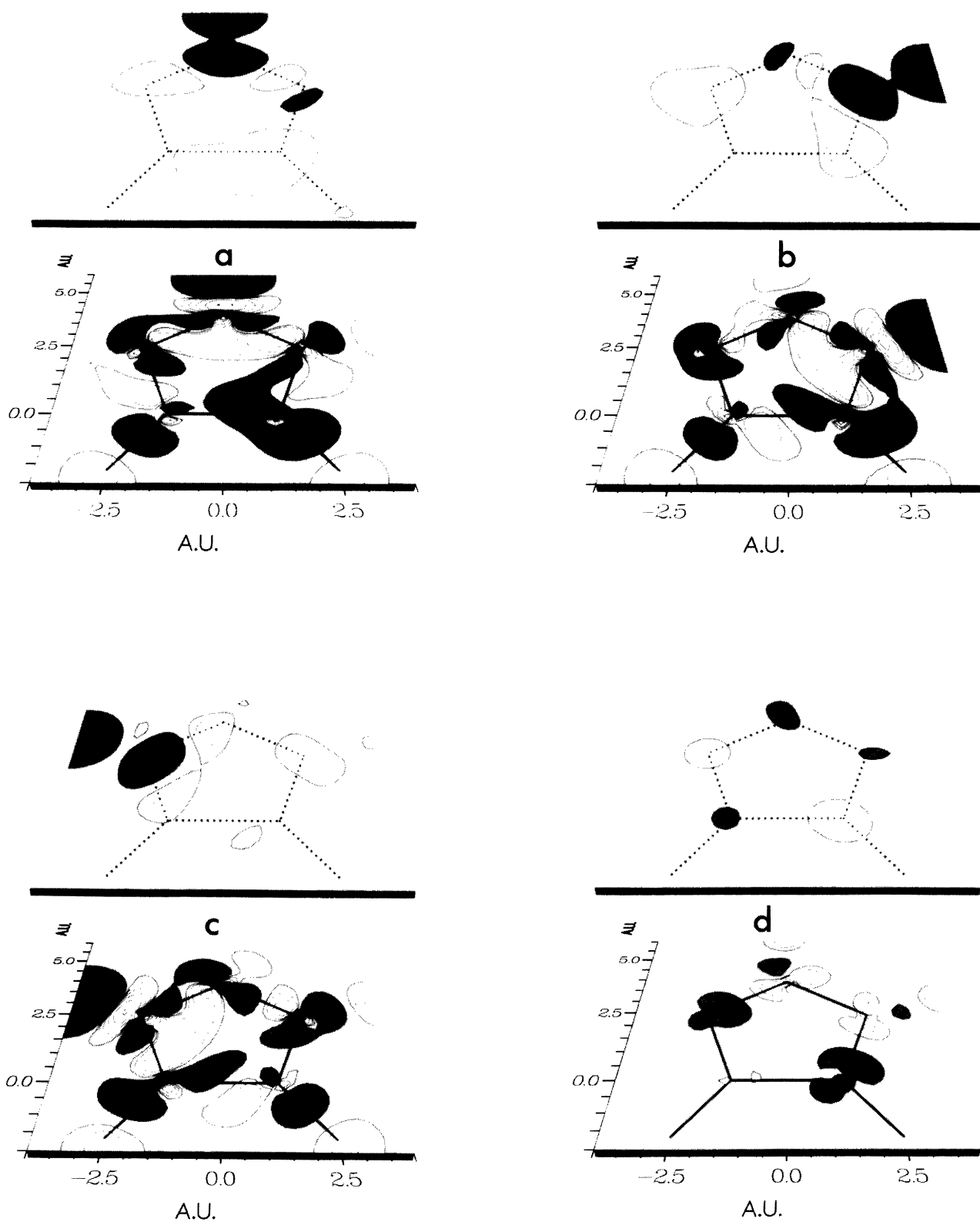


Fig. 3. Difference densities between T12 and T1 (a) and T2 (b), and T13 and T1 (c). Fig. 3d depicts the difference between Fig. 3b and Fig. 2a.

Table 2. Gross charges, q , and overlap populations, o , from Mulliken population analysis.

	T0	T1	T2	T12	T13
$q(\text{N1})$	-0.253	-0.180	-0.135	-0.136	-0.128
$q(\text{N2})$	-0.211	-0.096	-0.140	-0.108	0.043
$q(\text{N3})$	-0.253	-0.140	-0.135	0.014	-0.128
$q(\text{C4})$	-0.177	-0.086	-0.075	-0.020	0.013
$q(\text{C5})$	-0.177	-0.066	-0.075	0.083	0.013
$o(\text{N1-N2})$	0.815	0.595	0.646	0.486	0.768
σ/π^a	0.547/0.268	0.425/0.170	0.498/0.148	0.444/0.042	0.531/0.237
$o(\text{N2-N3})$	0.815	0.920	0.646	0.730	0.768
σ/π^a	0.547/0.268	0.604/0.316	0.498/0.148	0.539/0.191	0.531/0.237
$o(\text{N3-C4})$	1.129	1.026	1.222	1.108	0.835
σ/π^a	0.822/0.307	0.766/0.260	0.838/0.384	0.769/0.339	0.630/0.205
$o(\text{C4-C5})$	1.128	1.178	0.990	0.996	1.193
σ/π^a	0.795/0.333	0.774/0.404	0.729/0.261	0.692/0.304	0.787/0.406
$o(\text{C5-N1})$	1.129	0.852	1.222	1.006	0.835
σ/π^a	0.822/0.307	0.652/0.200	0.838/0.384	0.716/0.290	0.630/0.205

^aPartitions into σ - and π -contributions.

Table 3. The s-electron population of the ring atoms.

	T0	T1	T2	T12	T13
s(N1)	3.576	3.432	3.603	3.442	3.449
s(N2)	3.667	3.678	3.455	3.455	3.680
s(N3)	3.576	3.621	3.603	3.649	3.449
s(C4)	3.130	3.154	3.156	3.176	3.164
s(C5)	3.130	3.144	3.156	3.169	3.164

Table 4. Model 1: a property, p , described as a linear function of up to three variables, v_i , for the five different molecules; the model constitutes five equations with three parameters.

Compound	Equation
T0	$p = v_0$
T1	$p = v_0 + v_1$
T13	$p = v_0 + 2v_1$
T2	$p = v_0 + v_2$
T12	$p = v_0 + v_1 + v_2$

Table 5. Model 2: the model takes into account the asymmetry of N1 and C5 on one side and N3 and C4 on the other (for T1 and T12 this results in two equations involving either N1/C5 or N3/C4); the model constitutes seven equations with four parameters.

Compound	Equation
T0	$p = v_0$
T1	$p(\text{N1/C5}) = v_0 + v_1$ $p(\text{N3/C4}) = v_0 + v_3$
T13	$p = v_0 + v_1 + v_3$
T2	$p = v_0 + v_2$
T12	$p(\text{N1/C5}) = v_0 + v_1 + v_2$ $p(\text{N3/C4}) = v_0 + v_2 + v_3$

Table 6. Model 1 applied to the C-C overlap population, o ,^a and the sum of the charges, q ,^b at the two carbon atoms.

Compound	$o(\text{C4,C5})$	Deviation	$q(\text{C4} + \text{C5})$	Deviation
T0	1.128	-0.011	-0.355	0.001
T1	1.178	0.012	-0.152	0.008
T2	0.990	0.011	-0.151	-0.009
T12	0.996	-0.011	0.063	0.009
T13	1.193	-0.001	0.026	-0.009
R.m.s.		0.010		0.008

^a $o(\text{C4,C5})$: $v_0 = 1.139$, $v_1 = 0.027$, $v_2 = -0.160$.

^b $q(\text{C4} + \text{C5})$: $v_0 = -0.355$, $v_1 = 0.195$, $v_2 = 0.214$.

however, obtained for the s-populations at C4,C5 and N1,N3 (Table 7). A model 1 analysis of the s-population at N2 gave an r.m.s. of 0.002.

Additivity in orbital energies. Model 1 has, with good agreements, been applied to the energies of the three π -orbitals, the three lowest 2s-orbitals and the energies of the lowest unoccupied molecular orbital (LUMO). Table 8 shows the results for the highest occupied π -orbital (HOMO) and LUMO. The root mean square

Table 7. Model 2 analysis of the s-population: deviations from calculated populations.

	s(N1,N3)	s(C4,C5)
T0	-0.005	-0.0013
T1(N1/C5)	0.012	0.0018
T1(N3/C4)	0.002	0.0004
T2	-0.003	0.0004
T12(N1/C5)	-0.003	-0.0009
T12(N3/C4)	0.006	0.0005
T13	-0.008	-0.0009
R.m.s.	0.006	0.0010

Table 8. Model 1 applied to the orbital energies (a.u.), ϵ , of HOMO^a and LUMO.^b

Compound	$\epsilon(\text{HOMO})$	Deviation	$\epsilon(\text{LUMO})$	Deviation
T0	-0.124 280	0.0011	0.395 783	-0.0019
T1	-0.352 869	-0.0014	0.132 331	-0.0045
T2	-0.386 388	-0.0008	0.129 254	0.0007
T12	-0.610 969	0.0008	-0.129 085	0.0007
T13	-0.577 298	0.0003	-0.117 542	0.0026
R.m.s.		0.0010 $\sim 0.64 \text{ kcal mol}^{-1}$		0.0025 $\sim 1.55 \text{ kcal mol}^{-1}$

^aHOMO: $v_0 = -0.125\ 359$, $v_1 = -0.226\ 123$, $v_2 = -0.260\ 258$. ^bLUMO: $v_0 = 0.393\ 855$, $v_1 = -0.256\ 998$, $v_2 = -0.265\ 272$.

deviations are equal to $0.64 \text{ kcal mol}^{-1}$ (HOMO) and $1.55 \text{ kcal mol}^{-1}$ (LUMO). These energy differences are of the same order of magnitude as van der Waals energies. The two orbitals play an important role for the prediction of the site of substitution. For HOMO the distribution of charges may give a lead to the position of electrophilic substitution. However, application of model 1 or 2 to the gross charges and net populations of the carbon atoms or the nitrogen atoms failed and clearly showed the inadequacy of the model. The only result obtained with a reasonable accuracy was application of model 1 to the sum of the net atomic population of the nitrogen atoms. The HOMO possesses a node plane close to N1 and N3, giving low values of the net atomic population at the two atoms.

The accuracy of the additivity for the remaining five orbitals is of the same order as for LUMO. When ordered in an increasing sequence, there is a high degree of correlation between a pair of $2s$, π -orbital energies. The

correlation coefficients range from 0.999 75 to 0.999 92. A correlation coefficient of 0.999 98 is obtained between the energies of LUMO and the lowest π -orbital.

Relation to the empirical correlations. The correlations found in Ref. 1 have been related to changes in hybridization. However, it is difficult, directly on basis of the delocalized orbitals obtained by the present SCF-method, to find quantities expressing the degree of hybridization of the atoms. A closer examination of the results from the population analyses indicates that the total number of s -electrons at N1 and N3 to some degree depicts the average degree of hybridization of the two atoms: Model 2 analysis gives a good description, and the correlation coefficient between this set of numbers and the sum of σ -contributions to the overlap populations C5-N1 and C4-N3 is reasonably high (0.98). This sum of s -electrons may be related to the sum of the endocyclic angles at the carbon atoms. The dependence is shown in Fig. 4. The r.m.s. of the deviations from the least-squares line is 0.20° , and thus of the same order of magnitude as the standard deviations of the angles. The agreement is surprisingly good, keeping in mind that apart from hydrogen atom positions the two sets of numbers are obtained in two completely independent ways.

Conclusion

Several quantities obtained by the present model calculations obey, more or less accurately, the rule of additivity in the substitution effects. The link to the notion of hybridization is, however, difficult to establish because of the delocalized character of the orbitals. Qualitatively, the difference densities in the molecular plane show a behaviour similar to the changes in hybridization, and the very accurate description of the additive changes in the s -population of the ring atoms supports the idea of attributing the changes in the ring geometry to changes in hybridization. The correlations described in Ref. 1 and in the present paper indicate that it may be possible to find a set of correlations from which both geometrical and electronic properties may be predicted for unknown triazoles.

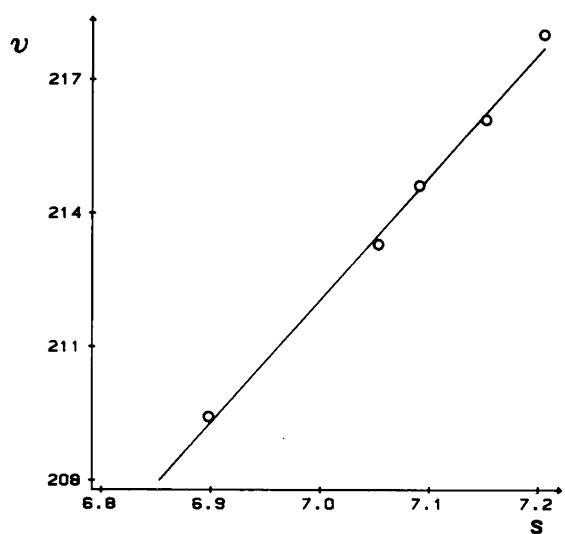


Fig. 4. The average angular sum, v (in $^\circ$), of the angles at the carbon atoms depicted as a function of the sum, s , of the s -electrons at N1 and N3.

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