Chemistry of Heterocyclic Compounds, Vol.35, No. 6, 1999

ab initio CALCULATIONS OF THE ELECTRONIC EFFECTS IN CHLOROPYRIMIDINES AND CHLOROPYRAZINES

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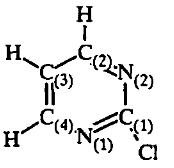
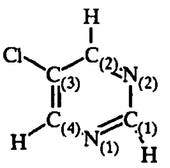
RHF/6-31G(d) calculations for 2- and 5-chloropyrimidines and 2-chloropyrazine show alternation of charge and π-electron density on the ring atoms in the pyrimidine derivatives and absence of such alternation in the pyrazine derivative. This finding is in accord with bond polarization by the charge of the geminal atom directly through space. The ^{35}Cl NQR frequencies estimated from the calculation data for these molecules were similar to the experimental values.

The results of *ab initio* calculations for pyridine and chloropyridines have shown that the negatively charged nitrogen atom causes alternation of the charges and π-electron density on the ring carbon atoms and also a lower ^{35}Cl NQR frequency for 2-chloropyridine than for 3-chloropyridine and chlorobenzene due to polarization of the C–C and C–Cl bonds by the charge of the nitrogen or carbon atom in the geminal position in these molecules [1]. We have now studied these effects in chlorodiazines containing two strongly electronegative nitrogen atoms in the ring. For this purpose, *ab initio* calculations were carried out for 2-chloropyrimidine (I), 5-chloropyrimidine (II), and 2-chloropyrazine (III) with complete geometrical optimization.

These molecules were selected for study since their experimental ^{35}Cl NQR frequencies have been reported and may be compared with the calculated results. These restricted Hartree–Fock calculations with the 6-31G(d) split valence basis were carried out using the Gaussian-92 program (Gaussian Inc.) [2]. The origin for all these molecules was selected as the site of the chlorine nucleus. The *z*-axis is along the C–Cl bond, while the *y*-axis is perpendicular to the molecular plane.



I



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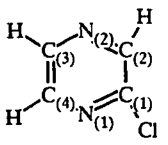

III

The results for optimization of the geometry of I–III indicated that all these molecules are planar. The dihedral angles are equal to 0° or 180°±0.02° (0.05° for III). The C–Cl and C–N bonds in all these molecules are slightly shorter than in chloropyridine (Table 1) [1], while the C–H bonds are virtually identical (1.074±0.02 Å). The greatest negative charges are found for the nitrogen atoms (Table 2). The nitrogen atoms in compounds I and II are in a geminal position relative to each other. Thus, in accord with the noninductive interaction of geminal atoms (see, for example, our previous work [1, 3]), these nitrogen atoms have greater negative charge than the nitrogen atoms in III.

Institute of Technical Chemistry, Urals Branch of the Russian Academy of Sciences, 61400 Perm, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 782-785, June, 1999. Original article submitted April 1, 1998.

0009-3122/99/3506-0695$22.00©1999 KluwerAcademic/Plenum Publishers

TABLE 1. Bond Lengths (*d*) and Angles (α) in Molecules of Compounds I–III from RHF/6-31(d) Calculations

Bond	*d*, Å		
	I	II	III
C–Cl	1.731	1.732	1.734
$N_{(1)}$–$C_{(1)}$	1.310	1.318	1.301
$N_{(2)}$–$C_{(2)}$	1.322	1.318	1.312
$C_{(2)}$–$C_{(3)}$	1.381	1.381	—
$C_{(3)}$–$C_{(4)}$	1.381	1.381	1.380
$C_{(4)}$–$N_{(1)}$	1.322	1.318	1.323
$C_{(3)}$–$N_{(2)}$	—	—	1.324

Bond angle	α, deg		
	I	II	III
$N_{(1)}C_{(1)}Cl$	116.1	—	118.0
$C_{(1)}N_{(1)}C_{(4)}$	115.8	116.8	116.5
$N_{(1)}C_{(4)}C_{(3)}$	122.4	121.4	121.3
$C_{(2)}C_{(3)}C_{(4)}$	115.7	—	—
$N_{(2)}C_{(2)}C_{(3)}$	122.4	—	—
$ClC_{(3)}C_{(4)}$	—	121.4	—
$N_{(1)}C_{(1)}N_{(2)}$	—	126.5	—
$C_{(1)}N_{(2)}C_{(2)}$	—	116.8	—
$N_{(2)}C_{(3)}C_{(4)}$	—	—	121.6
$C_{(2)}N_{(2)}C_{(3)}$	—	—	117.4

TABLE 2. Atomic Charges (a. u.)

Molecule	$N_{(1)}$	$N_{(2)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	Cl
I	-0.493	-0.493	0.348	0.102	-0.304	0.102	0.044
II	-0.504	-0.505	0.261	0.122	-0.235	0.122	0.032
III	-0.451	-0.450	0.099	0.049	0.011	0.017	0.032

The nitrogen atoms in heterocycles I and II polarize the geminal $C_{(2)}$–$C_{(3)}$ and $C_{(4)}$–$C_{(3)}$ bonds such that a negative charge arises on $C_{(3)}$ and positive charges arise on $C_{(2)}$ and $C_{(4)}$, i.e., charge alternation occurs for the carbon and nitrogen atoms of the pyrimidine ring. The negative charge on $C_{(3)}$ in 2-chloropyrimidine I is somewhat greater than in II since electron density is not drawn off from this atom by the chlorine atom. All the pyrazine ring carbon atoms in III have small positive charge as the result of the inductive effect of the nitrogen atoms and compensation of the noninductive effects of the two nitrogen atoms directly through space on the geminal C–C bond.

The occupancies of the p_y-orbitals of the nitrogen and carbon atoms in the planar structures of I–III (Table 3) characterize their π-electron density. An excess of π-electron density in molecules I and II is found for the nitrogen and $C_{(3)}$ atoms, while a deficit is found on the other carbon atoms and chlorine atom. Thus, the π-electron density deficit or excess on the carbon and nitrogen atoms alternate similarly to the charges. The atomic charge probably polarizes not only the geminal σ-bond directly through space but also the corresponding π-component. Such alternation of charge and π-electron density on ring atoms is especially pronounced in pyridine [1]. Excess π-electron density is observed in all nitrogen heterocyclic compounds on the nitrogen atom. This excess π-electron density corresponds to the greater electronegativity of nitrogen relative to other atoms. All the carbon atoms in III have a π-electron density deficit.

In accord with the noninductive effect of an atom M on the indicator atom Y in the Y–C–M and Y–C=M groups, entailing polarization of the C–Y bond by the charge of atom M directly through space (see, for example, our previous work [3]), we may propose that the ^{35}Cl NQR frequency in I will be lower than in II, which is actually

TABLE 3. Occupancies (a. u.) of the p_y-Orbitals of Carbon and Nitrogen Atoms

Molecule	$N_{(1)}$	$N_{(2)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$
I	1.192	1.192	0.867	0.820	1.072	0.820
II	1.173	1.173	0.819	0.833	1.116	0.833
III	1.096	1.068	0.979	0.936	0.946	0.929

observed: the experimental ^{35}Cl NQR frequency of compound I at 77 K is 34.470 MHz, while it is 36.123 MHz for 5-chloropyrimidine II [4]. We have shown that the ^{35}Cl NQR frequencies and electric field gradient asymmetry parameters on ^{35}Cl nuclei in organic and heteroorganic molecules may be evaluated using Eq. (1) and the occupancies of the 3*p*-components of the chlorine atom valence *p*-orbitals found from the *ab initio* calculations for these molecules in the split 6-31G(d) valence basis (see, for example, our previous work [1, 3, 5]). This permits us to elucidate the reason for the relationship of the NQR frequencies.

The ^{35}Cl NQR frequencies for derivatives I and II calculated by this method given in Table 4 are similar to the experimental values. The lower ^{35}Cl NQR frequency of I relative to II is due to the higher occupancy of the 3*p*-component of the chlorine atom valence p_z-orbital in compound I (Table 4).

$$\nu = (e^2Qq_{at}/2h)[(Np_x + Np_y)/2 - Np_z](1 + \eta^{2/3})^{1/2} \quad (1)$$

Some contribution to the ^{35}Cl NQR frequency is made by the half-sum of the occupancies of the 3*p*-components of the chlorine atom p_x- and p_y-orbitals (Eq. (1)). However, in compound II this half-sum is even less than in analog I, which should lead to a reverse relationship of ^{35}Cl NQR frequencies. Therefore, it is not responsible for the lower ^{35}Cl NQR frequency of I relative to II. This finding is in accord with the explanation of the anomalous variation in the ^{35}Cl NQR frequencies in a series of compounds with a Cl–C=M group (with variation in M) due to polarization of the C–Cl bond by the charge of atom M directly through space (see, for example, our previous work [3, 6, 7]).

The experimental ^{35}Cl NQR frequency for III (35.049 MHz [4]) is also close to the value calculated using its occupancies of the 3*p*-components of the chlorine atom valence *p*-orbitals (Table 4) but higher than for I as should have been expected on the basis of the behavior of the noninductive effect of atom M on the indicator chlorine atom in the Cl–C=M group discussed above. Unfortunately, the relationship of the ^{35}Cl NQR frequencies evaluated for these molecules is opposite to the experimental relationship since the calculated ^{35}Cl NQR frequency for I appears to be somewhat overestimated, while it is somewhat underestimated for III relative to the corresponding experimental value. The occupancies of the 3*p*-components of the chlorine atom valence p_z-orbitals in I and III are identical. The difference in the estimated NQR frequencies of these molecules is a consequence only of slight disagreement of the half-sums for the 3*p*-components of the p_x- and p_y-orbitals of their chlorine atoms (1.316 and 1.314 MHz, respectively).

The ^{35}Cl NQR frequencies of compounds I–III calculated using the total occupancies of the chlorine atom valence *p*-orbitals or their more diffuse components differ significantly from the experimental values (Table 4), as in the case of other chlorine-containing systems (see, for example, our previous work [1, 3, 5]). The electric field gradient asymmetry parameters on the ^{35}Cl nuclei in these molecules were not measured but may be estimated using the occupancies of the 3*p*-components of the chlorine atom valence *p*-orbitals. The asymmetry parameters thereby calculated are usually close to the experimental values [3, 5]. We may assume that this is also true for the compounds studied (Table 4). According to the estimates for I–III, the asymmetry parameters increase with accumulation of nitrogen atoms in the geminal positions relative to the chlorine atom.

TABLE 4. Occupancies of the Chlorine Atom Valence *p*-Orbitals (ΣNp, a. u.), Their 3*p*- and 4*p*-Components and Calculated ^{35}Cl NQR Frequencies (ν_B) and Asymmetry Parameters (η_B) on the ^{35}Cl Nuclei

Molecule	Orbital	N_x	N_y	N_z	ν_B, MHz	η_B, %
I	3*p*	1,337	1,295	0,941	35,117	16,7
	4*p*	0,625	0,645	0,170	61,969	6,6
	ΣNp	1,962	1,940	1.111	46,060	3,8
II	3*p*	1,318	1,311	0,932	35,624	2,9
	4*p*	0,641	0,646	0,172	62,828	1,4
	ΣNp	1,959	1,957	1,104	46,811	0,5
III	3*p*	1,326	1,302	0,941	34,762	9,6
	4*p*	0,633	0,646	0,175	61,954	4,2
	ΣNp	1,959	1,948	1,116	45,912	1,9

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