Effect of substituents in the ring on the structure and electron density distribution in benzyl halides

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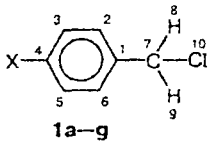
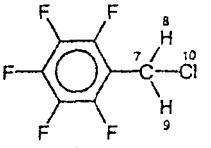
The results of calculations for benzyl chlorides and benzyl bromides that contain substituents in the ring by different quantum-chemical methods are compared. The electron density on the benzyl carbon atom increases as the electron-withdrawing properties of substituents are enhanced due to the shift of the electron density from the benzyl halogen atom to the adjacent carbon atom. A topological analysis according to Bader confirmed the main reason for the change in the paramagnetic shielding of the benzyl ^{13}C nuclei. The results of calculations provide, for the first time, an explanation for the resonance upfield ^{13}C shift of this atom as the Hammett constant of a substituent increases in compounds of the series under consideration.

Key words: benzyl chlorides, benzyl bromides, electronic structure, *ab initio* calculations, semiempirical calculations, ^1H NMR, ^{13}C NMR.

The effect of substituents on the structures, properties, and reactivities of organic compounds is one of the most important problems of organic chemistry.[1—6]



1a—g



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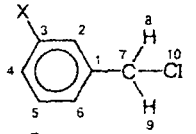

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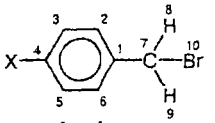

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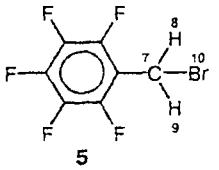

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1: X = MeO (**a**), Me (**b**), H (**c**), F (**d**), Cl (**e**), CF_3 (**f**), NO_2 (**g**)
3: X = Me (**a**), H (**b**), MeO (**c**), F (**d**), Cl (**e**), CF_3 (**f**), NO_2 (**g**)
4: X = MeO (**a**), Me (**b**), H (**c**), F (**d**), Cl (**e**), CF_3 (**f**), CN (**g**), NO_2 (**h**)

Benzyl halides, which are reagents in organic synthesis, are widely used in studies of mechanisms of reactions.[7—10] However, the electronic structures of benzyl halides and the effect of X substituents on the electron density distribution have not been adequately studied. For example, it was suggested that stronger electron acceptors X favor an increase in the positive charge, *i.e.*, a decrease in the electron density on the benzyl carbon atom,[11,12] and promote interaction between a nucleophile and this atom.[11]

In this work, we studied the effect of substituents on the structure and electron density distribution in benzyl halides (**1**—**5**) by *ab initio* and semiempirical quantum-chemical calculations and by NMR spectroscopy. Because the reaction center in these compounds is generally the benzyl C(7) atom, in this work primary attention was given to the study of changes in the electronic structure which occur in the region of this center, as well as of changes in the electron density on the C(7) atom, the adjacent halogen atoms, and other atoms.

Experimental

Benzyl halides (Aldrich) were used without additional purification. The ^1H NMR (400 MHz) and ^{13}C (100.6 MHz) spectra of solutions of benzyl halides in CD_2Cl_2 (~0.4 mol L^{-1}) were recorded on a VXR-400 spectrometer (Varian) with TMS as the internal standard.

The *ab initio* RHF 6-31G calculations of *para*-substituted benzyl chlorides were carried out using the GAMESS program.[13] The semiempirical quantum-chemical calculations of benzyl halides were performed using the MNDO[14,15] and PM3[16] methods, which were realized in the MOPAC 6.00 program package[17] adapted to a PC computer. Both *ab initio* and semiempirical calculations were carried out with full geometry optimization. The exception was the MNDO calculation of benzyl bromide **4h** with the planar conformation of the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2111—2119, December, 1997.

1066-5285/97/4612-1996$18.00

Table 1. Total energies (E/Hartree), heats of formation (Δ_fH/kcal mol^{-1}), energies of HOMO (E_{HOMO}/eV) and LUMO (E_{LUMO}/eV), bond lengths (d/Å), and bond orders (n) for *para*-substituted benzyl chlorides **1** and pentafluorobenzyl chloride **2** calculated by the RHF/6-31G, MNDO, and PM3 methods

Compound	σ_p[a]	E (Δ_fH)	E_{HOMO}	E_{LUMO}	$d_{C(1)-C(7)}$	$d_{C(7)-Cl(10)}$	$n_{C(1)-C(7)}$	$n_{C(7)-Cl(10)}$
				RHF 6-31G				
1a	−0.27	−842.35312	−8.7	3.0	1.487	1.909	0.906	0.933
1b	−0.17	−767.54813	−9.0	2.9	1.489	1.905	0.902	0.936
1c	0.00	−728.52632[b]	−9.3	2.9, 1.535[c]	1.492, 1.802[c]	1.897	0.894	0.944
1d	0.06	−827.34982	−9.6	2.6	1.490	1.899	0.901	0.944
1e	0.23	−1187.40235	−9.6	2.4	1.491	1.896	0.898	0.948
1f	0.54	−1064.03813	−10.2	1.9	1.493	1.890	0.893	0.954
1g	0.78	−931.87658	−10.5	0.6	1.494	1.887	0.892	0.958
2	0.86[d]	−1222.59068	−11.2	1.4	1.489	1.876	0.886	0.972
				MNDO				
1a		(−35.1)	−9.1	−0.3	1.498	1.814	0.991	0.906
1b		(−3.4)	−9.5	−0.4	1.501	1.812	0.988	0.910
1c		(−7.8)	−9.6	−0.3	1.506	1.807	0.977	0.930
1d		(−41.9)	−9.7	−0.7	1.501	1.812	0.988	0.913
1e		(−2.9)	−9.8	−0.7	1.502	1.810	0.986	0.915
1f		(−143.4)	−10.3	−1.1	1.503	1.808	0.984	0.921
1g		(22.2)	−10.5	−1.6	1.504	1.806	0.983	0.924
2		(−212.7)	−10.6	−2.1	1.510	1.804	0.978	0.931
				PM3				
1a		(−26.8)	−9.2	0.0	1.483	1.790	1.003	0.959
1b		(2.1)	−9.5	−0.0	1.484	1.786	1.000	0.966
1c		(11.43)	−9.8	−0.1	1.483	1.788	1.002	0.961
1d		(−31.9)	−9.8	−0.3	1.486	1.779	0.996	0.973
1e		(4.9)	−9.4	−0.3	1.485	1.785	0.9999	0.968
1f		(−146.4)	−10.4	−0.8	1.486	1.782	0.998	0.971
1g		(3.3)	−10.6	−1.4	1.486	1.781	0.998	0.973
2		(−197.4)	−10.6	−1.5	1.485	1.780	0.995	0.974

[a] See Ref. 21. [b] According to 6-31G//3-21G calculations, the total energy of benzyl chloride with the perpendicular conformation of the chloromethyl group is −728.52605 Hartree.[22] [c] See Ref. 23. [d] $\sigma = 2\sigma_o + \sigma_p + 2\sigma_m$.[12]

NO_2 group. In this case, the C(3)—C(4)—N—O torsion angle was fixed equal to 0°. The critical points, electron density, charges on atoms, and other properties of atoms within the framework of Bader's theory[18,19] were determined using the AIMPAC program.[20]

Results and Discussion

The total energies E (6-31G) and heats of formation Δ_fH (MNDO and PM3) for seven *para*-substituted benzyl chlorides **1** and pentafluorobenzyl chloride **2** are given in Table 1. The heats of formation of *meta*-substituted benzyl chlorides **3**, *para*-substituted benzyl bromides **4**, and pentafluorobenzyl bromide **5** calculated by the semiempirical methods are given in Tables 2 and 3.

The heats of formation of benzyl halides **1c** and **4c** calculated by the MNDO method are in better agreement with the experimental values reported in the literature (see Tables 1 and 3, respectively) than the heats of formation calculated by the PM3 method. The data in Tables 1—3 demonstrate that the MNDO and PM3 methods gave substantially different estimations of the heats of formation of benzyl halides.[16,25]

According to the results of RHF 6-31G and MNDO calculations, the energetically most stable conformation of benzyl chlorides **1** and **2** is the conformation in which the benzyl Cl(10) atom lies in the plane almost perpendicular to the plane of the benzene ring. The C(2)—C(1)—C(7)—Cl(10) torsion angle (θ) is 88—90°. This result agrees well with the evidence that perpendicular conformations are more stable in the case of **1c**,[22,26,27] **1e**,[28] and a number of substituted toluenes $ArCH_2X$.[26] The energetically most stable conformers with the halide atom located in the plane perpendicular (or almost perpendicular) to the plane of the benzene ring were predicted by the MNDO method for compounds **3** (θ = 86—90°), **4**, and **5** (θ = 84—90°), whereas the PM3 calculations led to conformers with skewed orientation of the Cl(10) atom with respect to the plane of the benzene ring in the case of compounds **1b**, **1d—g**, **2**, **3f**, and **3g** (or of the Br(10) atom in the case of **4a**, **4c—h**,

Table 2. Heats of formation ($\Delta_f H$/kcal mol^{-1}), energies of HOMO (E_{HOMO}/eV) and LUMO (E_{LUMO}/eV), bond lengths (d/Å), and bond orders (n) for *meta*-substituted benzyl chlorides **3** calculated by the MNDO and PM3 (in parentheses) methods

Compound	σ_p [a]	$\Delta_f H$	E_{HOMO}	E_{LUMO}	$d_{C(1)-C(7)}$	$d_{C(7)-Cl(10)}$	$n_{C(1)-C(7)}$	$n_{C(7)-Cl(10)}$
3a	−0.07	−3.3 (2.2)	−9.5 (−9.6)	−0.3 (−0.0)	1.501 (1.482)	1.812 (1.787)	0.988 (1.002)	0.910 (0.961)
3b	0.00	−7.8 (11.4)	−9.7 (−9.8)	−0.3 (−0.1)	1.501 (1.483)	1.812 (1.788)	0.988 (1.002)	0.910 (0.961)
3c	0.12	−34.8 (−26.3)	−9.5 (−9.3)	−0.4 (−0.1)	1.501 (1.485)	1.812 (1.788)	0.987 (1.001)	0.911 (0.962)
3d	0.34	−41.4 (−31.8)	−9.7 (−9.9)	−0.6 (−0.4)	1.503 (1.485)	1.810 (1.786)	0.985 (1.000)	0.916 (0.964)
3e	0.37	−2.8 (4.9)	−9.8 (−9.5)	−0.6 (−0.3)	1.503 (1.484)	1.808 (1.787)	0.986 (1.001)	0.916 (0.963)
3f	0.43	−143.5 (−146.4)	−10.3 (−10.3)	−1.0 (−0.7)	1.503 (1.485)	1.809 (1.783)	0.985 (0.998)	0.918 (0.970)
3g	0.71	20.4 (3.4)	−10.5 (−10.5)	−1.2 (−1.2)	1.504 (1.486)	1.808 (1.781)	0.984 (0.996)	0.921 (0.973)

[a] See Ref. 21.

Table 3. Heats of formation ($\Delta_f H$/kcal mol^{-1}), energies of HOMO (E_{HOMO}/eV) and LUMO (E_{LUMO}/eV), bond lengths (d/Å), and bond orders (n) for *para*-substituted benzyl bromides **4** and pentafluorobenzyl bromide **5** calculated by the MNDO and PM3 (in parentheses) methods

Compound	σ_p [a]	$\Delta_f H$	E_{HOMO}	E_{LUMO}	$d_{C(1)-C(7)}$	$d_{C(7)-Br(10)}$	$n_{C(1)-C(7)}$	$n_{C(7)-Br(10)}$
4a	−0.27	−23.4 (−16.1)	−9.0 (−9.2)	−0.3 (−0.5)	1.496 (1.469)	1.897 (1.966)	0.996 (1.021)	0.930 (0.927)
4b	−0.17	8.1 (12.2)	−9.4 (−9.4)	−0.4 (−0.6)	1.497 (1.468)	1.896 (1.969)	0.994 (1.026)	0.933 (0.921)
4c	0.00	15.9, 15.1[b], 3.8, 7.1 (22.1)	−9.6 (−9.7)	−0.3 (−0.6)	1.498, 1.528[c] (1.472)	1.895 1.978[c] (1.964)	0.993 (1.018)	0.933 (0.933)
4d	0.06	−30.3 (−21.3)	−9.6 (−9.8)	−0.7 (−0.8)	1.498 (1.472)	1.895 (1.962)	0.993 (1.017)	0.935 (0.935)
4e	0.23	8.6 (15.2)	−9.8 (−9.4)	−0.7 (−0.7)	1.499 (1.472)	1.894 (1.962)	0.992 (1.017)	0.937 (0.935)
4f	0.54	−132.0 (−135.7)	−10.2 (−10.4)	−1.1 (−1.1)	1.500 (1.473)	1.891 (1.958)	0.990 (1.013)	0.942 (0.944)
4g	0.66	47.3 (57.7)	−9.4 (−10.0)	−1.0 (−1.1)	1.499 (1.473)	1.893 (1.959)	0.991 (1.015)	0.939 (0.941)
4h$_{\parallel}$[d]	0.78	33.5 (14.1)	−10.5 (−10.6)	−1.6 (−1.5)	1.501 (1.475)	1.891 (1.956)	0.989 (1.012)	0.944 (0.947)
4h$_{\perp}$[e]	0.78	31.7	−10.5	−1.3	1.501	1.891	0.989	0.943
5	0.86[f]	−201.4 (−187.4)	−10.5 (−10.6)	−2.0 (−1.7)	1.506 (1.473)	1.889 (1.955)	0.984 (1.011)	0.950 (0.952)

[a] See Ref. 21. [b] The experimental heat of formation of benzyl bromide[24]. [c] See Ref. 23. [d] In **4h**$_{\parallel}$, the NO_2 group lies in the plane parallel to the plane of the benzene ring. [e] In **4h**$_{\perp}$, the plane of the NO_2 group is perpendicular to the plane of the benzene ring. [f] $\sigma = 2\sigma_o + \sigma_p + 2\sigma_m$.[12]

and **5**). In the above-mentioned *para*- and *meta*-substituted benzyl chlorides, the C(2)—C(1)—C(7)—Cl(10) torsion angle varies from 56 to 61°, which is close to the value (67.5°) determined by electron diffraction study of one of the possible conformers of **1c**.[23] In benzyl bromides **4a**, **4c**—**h**, and **5**, the C(2)—C(1)—C(7)—Br(10) torsion angle varies, according to PM3 calculations, from 53 to 59°. Only for compounds **1a**, **1c**, **3a**—**e**, and **4b** did the PM3 method give the results (θ = 89, 90, 90, 89, 88, 86, 85, and 89°, respectively) that correlate with

the results of *ab initio* (**1a** and **1c**) and MNDO calculations as well as with the results of electron diffraction study for the second possible conformer of **1c** with $\theta = 90°$.[23]

In the case of benzyl chloride **1a** and benzyl bromide **4a**, all methods used predicted a conformation of the MeOPh fragment such that the MeO group deviates from the plane of the benzene ring by 1.0—1.8° (depending on the method of calculation). The arrangement of the MeO group in the plane of the benzene ring favors its maximum resonance interaction with the ring,[29] although it is associated with particular steric hindrances, which is evidenced by the values of the calculated C(3)—C(4)—O and C(5)—C(4)—O bond angles. In *meta*-substituted benzyl chloride **3c** in which the resonance interaction of the MeO group should not play a substantial role, this group, according to the results of MNDO calculations, is nearly perpendicular to the plane of the benzene ring. The C(2)—C(3)—O—C(Me) torsion angle is 76.9°. This agrees with the results of statistical analysis of conformations of the methoxyphenyl fragments.[29]

For compounds **1g** and **3g**, all methods used predicted that the NO_2 group lies in the plane parallel to the plane of the benzene ring. The parallel conformation of the NO_2 group also occurs, according to PM3 calculations, in compound **4h** (**4h**$_{\parallel}$). These results agree with the somewhat higher energetic stability of nitrobenzene and its substituted derivatives[30,31] with the coplanar geometry of the NO_2 group. However, according to MNDO calculations, the NO_2 group in the energetically more stable (by 1.8 kcal mol^{-1}) conformer of **4h** lies in the plane nearly perpendicular to the plane of the benzene ring. In this conformer (**4h**$_{\perp}$), the C(3)—C(4)—N—O torsion angle is 88.7°. The results of calculations demonstrate that the difference in the arrangement of the NO_2 group in conformers **4h**$_{\parallel}$ and **4h**$_{\perp}$ has virtually no effect on the values of other geometric parameters (see Table 3) and on the electron density distribution in these conformers, which agrees with the results of other studies.[30] In spite of the similarity in the electron density distribution in **4h**$_{\parallel}$ and **4h**$_{\perp}$ calculated by the MNDO method, hereinafter we shall use the data on conformer **4h**$_{\parallel}$ in which the conformation of the NO_2 group is close to that observed in compounds **1g** and **3g**.

The lack of experimental data on bond lengths and bond angles for most of the benzyl halides under study makes it impossible to judge whether the molecular geometries of the compounds under study are adequately described by the RHF 6-31G, MNDO, and PM3 methods. However, a comparison of the results of calculations of benzyl chloride **1c** and benzyl bromide **4c** with the experimental data demonstrated that, on the whole, the methods used make it possible to reliably predict the geometric parameters of benzyl halide molecules.

According to calculations, the electron-withdrawing properties of substituents increase in the series of benzyl chlorides **1a—g**, **2** (see Table 1), and **3a—g** (see Table 2) and benzyl bromides **4a—h** and **5** (see Table 3), which results in the distinct, although weak, tendencies, namely in an increase in the C(1)—C(7) bond length and a decrease in the bond length between the C(7) atom and the benzyl halogen atom (see Tables 1—3). The distinct, although slight, changes are also observed in the bond angles at the C(7) atom. In the above-mentioned series of benzyl halides, the C(7)—H(8) and C(7)—H(9) bond lengths calculated within the framework of the same method remain virtually unchanged. The observed changes in the geometry about the C(7) atom in benzyl halides are rather representative and are discussed below in more detail.

The effect of substituents on the electron density at the benzyl C atom is of most interest. The charges calculated according to Mulliken[32] and by the NBO method[33] for the RHF 6-31G wave function demonstrate that the total charge (hereinafter, "charge") q_7 on the C(7) atom has a large negative value in all benzyl chlorides **1** (Fig. 1) and **2** (q_7(Mulliken) = −0.4641 and q_7(NBO) = −0.4119), and it is several times higher than the charge q_{Cl} on the Cl(10) atom in these compounds calculated by the same methods (Fig. 2; in **2**, q_{Cl}(Mulliken) = −0.0280 and q_{Cl}(NBO) = −0.1078). The results obtained agree with the results of calculations for **1c** by the RHF 3-21G method.[22]

In benzyl chlorides **1** and **2**, the substantial increase in the electron density on the C(7) atom compared to the electron density on the benzyl Cl(10) atom is contradictory to the concept[34] of the lower electronegativity of the C atom compared to the Cl atom. On the other hand, the high negative values of q_7 in compounds **1** and

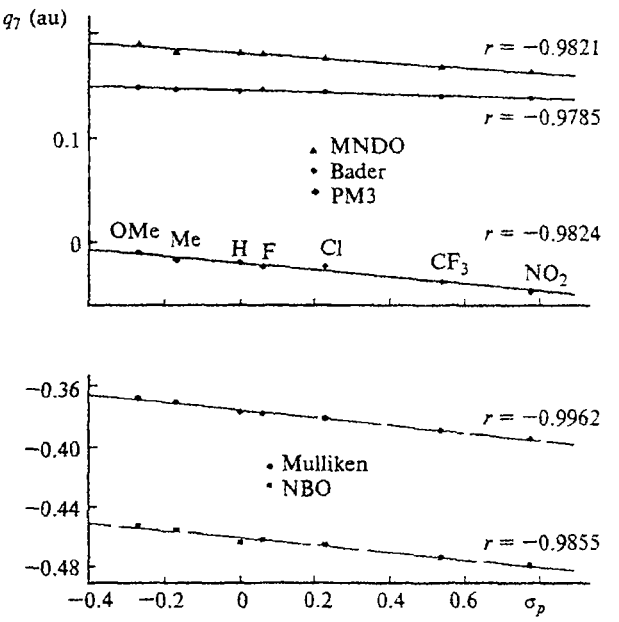

Fig. 1. Dependence of the calculated charges q_7 on the benzyl C(7) atom in benzyl chlorides **1a—g** and the values of the Hammett constant σ_p.

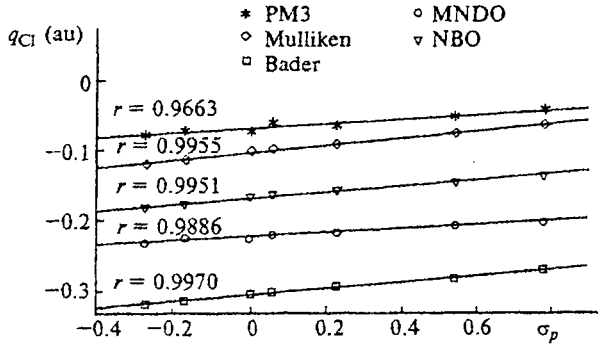

Fig. 2. Dependence of the calculated values of the charges q_{Cl} on the benzyl Cl(10) atom in benzyl chlorides **1a—g** on the values of the Hammett constant σ_p.

2, which were predicted by the analysis of occupancies according to Mulliken[32] and by the NBO method,[33] are completely inconsistent with the electrophilic properties of the benzyl C(7) center in the compounds under consideration.[1—7]

The disadvantages of the analysis of occupancies according to Mulliken, which result largely from the arbitrary partition of the electron density in the region of overlap of the electron shells of the atoms, are well known.[35] This may lead not only to a substantial overestimation of the calculated charge on the atom,[35] but to a wrong sign of the charge as well.[9,36] As can be seen from Figs. 1 and 2, the NBO method[33] may also give results that are inconsistent with the concept of the relative electronegativity[34] as well as with the electrophilic properties of the C(7) atom in benzyl chlorides.

Bader's approach to the determination of the electron density on atoms in molecules[18,19] is free from the drawbacks of Mulliken's method[32] and the NBO method[33] because the topological analysis[18] does not take into account the nature of orbitals[18,35,37] and depends to a substantially lesser degree on the size of the basis set.[18] Because of this, the topological analysis of the electron density distribution according to Bader with the use of the PROAIM program[20] gives better results[38] compared to alternative methods, and it is widely used in theoretical studies of the electron density distribution in molecules of various organic compounds.[9—11,18,30,37—41] The charges q_7 calculated according to Bader for all benzyl chlorides **1** (see Fig. 1) and benzyl chloride **2** (q_7 = 0.1704) are positive, whereas the charges q_{Cl} are negative (see Fig. 2; for benzyl chloride **2**, q_{Cl} = −0.2355). The values of the charges on the C(7) and Cl(10) atoms in compounds **1** and **2** are in complete agreement with the relative electronegativities of the C and Cl atoms[34] and with the tendency of benzyl halides to undergo nucleophilic substitution at the C(7) atom.

Calculations of charges according to Mulliken within the framework of the MNDO method[14,15] also gave positive values of q_7 in benzyl halides **1** and **2** (q_7(MNDO) = 0.1652), whereas the use of the PM3 method[16] led to small negative values of q_7 (see Fig. 1). An analogous relationship between the signs of the charges on the C(7) atom calculated by the MNDO and PM3 methods* is also observed in the case of benzyl chlorides **3**. In benzyl bromides **4** and **5**, q_7(MNDO) are positive (in **5**, q_7(MNDO) = 0.0823). The values of q_7(PM3) are positive in compounds **4a—e** and **4g** and negative in **4f**, **4h**, and **5**. Therefore, the MNDO and Bader's methods give an adequate estimate of the sign of the charge on the benzyl C atom in benzyl halides.

The data in Fig. 1 demonstrate that, in spite of the differences observed, all five methods used for calculations of the charges q_7 lead to the same tendency for a change in the electron density on the benzyl center in benzyl halides **1**, namely, *the electron density on the C(7) atom increases (!) linearly as the electron-withdrawing properties of the X substituent* (which are characterized by the Hammett constant σ_p[21]) *increase*. Therefore, the relationship between the value of q_7 on the benzyl C atom and σ_p can be described by Eq. (1):

$$q_Y = \rho_Y \sigma_i + b_Y, \qquad (1)$$

where $q_Y = q_7$, $\sigma_i = \sigma_p$, and the value of $\rho_Y = \rho_7$ is negative. When the charges were calculated according to Bader and by the MNDO method, the values of ρ_7, which characterize the sensitivity of a change in the charge on the C(7) atom to a change in the electronic properties of substituents (see Fig. 1), are −0.0099 and −0.0238, respectively.

The charges calculated according to Mulliken and by the NBO and PM3 methods are not considered below because they give negative values of q_7, which are inconsistent with the electrophilic properties of benzyl halides. The correlations based on these charges and the charges on other atoms lead to qualitative conclusions analogous to those obtained with the use of these values calculated according to Bader or by the MNDO method.

According to the results of semiempirical calculations (MNDO and PM3), in *meta*-substituted benzyl chlorides **3** and *para*-substituted benzyl bromides **4**, the electron density on the C(7) atom increases as the electron-withdrawing ability of substituents increases. This is evidenced by the negative values of ρ_7 (−0.0146 and −0.0235, respectively). In the case of calculations of q_7(MNDO) in benzyl halides **3** and **4**, the correlation coefficient r in Eq. (1) is 0.980 and 0.956, respectively. It should be noted that in going from **1g** to **2** and from **4h** to **5**, the electron density on the C(7) atom increases. However, the values of q_7 in compounds **2** and **5** calculated by any method used do not fit with the correlations q_7—σ_p for benzyl halides **1** and **4**, respectively. This is associated not only with incorrectness of the use of the total value of s for five F substituents in C_6F_5,[8] but with

* Hereinafter, by the MNDO and PM3 methods mentioned within the framework of the discussion of the charges on the atoms are meant calculations of charges according to Mulliken for the wave functions in the MNDO or PM3 approximations.

the *ortho* effect[42] of two F atoms on the electron density distribution in compounds **2** and **5** as well.

The increase in the electron density on the C(7) atom as the electron-withdrawing ability of substituents in benzyl halides increases is in contradiction with the change expected based on the general concepts of the effect of the properties of substituents on the electron density on the benzyl carbon atom.[11,12] However, the tendency for a change in the electron density on the benzyl C(7) atom, which was predicted by calculations, was confirmed by the data of ^{13}C NMR spectroscopy.

Actually, the analysis of the data given in Table 4 demonstrates that the resonance of the $^{13}C(7)$ nuclei in compounds **1** is linearly shifted upfield as the value of the Hammett constant σ ($r = 0.943$) increases. Analogous patterns are observed for benzyl halides **3** ($r = 0.979$) and **4** ($r = 0.967$). As expected,[43,44] the values r for compounds **1** and **4** are even higher (0.989 and 0.984, respectively) when the changes in the chemical shifts $\Delta\delta C(7)$ (relative to the chemical shift $\delta^{13}C(7)^0$ for the corresponding unsubstituted benzyl halide) are described by the two-parameter Hammett equation:[43,44]

$$\Delta\delta C(7) = \rho_I\sigma_I + \rho_R\sigma_R,$$

where σ_I and σ_R are the inductive and resonance components of the Hammett constant σ_p, respectively.[21] The constants $\rho_I = -2.4$ and $\rho_R = -1.1$, which characterize the sensitivity of a change in the chemical shift of the C(7) atom in benzyl chlorides **1** to the inductive and resonance effects of substituents, respectively, are also close to the values of these constants determined previously[43,44] for *para*-substituted benzyl chlorides (−2.4 and −0.9) and benzyl fluorides (−2.5 and −1.1). For benzyl bromides **4**, the constants ρ_I and ρ_R are −3.5 and −1.6, respectively. The negative values of ρ_I and ρ_R are indicative of the upfield shift of the resonance of the $^{13}C(7)$ nuclei as the electron-withdrawing properties of a substituent increase due both to the inductive and resonance effects.

Table 4. Chemical shifts (δ) for the C(1), C(7), and H(8, 9) atoms of benzyl halides **1**—**5**

Compound	C(1)	C(7)	H(8, 9)
1a	130.21	46.80	4.566
1b	135.11	46.79	4.567
1c	138.06	46.74	4.577
1d	134.11	45.96	4.577
1e	134.53	45.82	4.554
1f	142.06	45.62	4.631
1g	144.94	45.11	4.674
2	112.4	32.12	4.684
3a	137.96	46.86	4.554
3b	138.06	46.74	4.577
3c	139.48	46.69	4.559
3d	140.43	45.80	4.575
3e	139.98	45.73	4.555
3f	139.10	45.70	4.631
3g	139.95	45.18	4.687
4b	135.40	34.30	4.492
4c	138.42	34.11	4.514
4d	134.43	33.12	4.486
4f	142.45	32.38	4.528
4g	143.39	32.14	4.507
4h	145.42	31.58	4.549
5	112.7	16.64	4.516

The upfield shift of the resonance of the $^{13}C(7)$ nuclei in benzyl halides **1**, **3**, and **4** as the Hammett constant increases is indicative of an increase in the shielding constant of the $^{13}C(7)$ nuclei as the electron-withdrawing properties of the X substituent increase. The chemical shifts of the $^{13}C(7)$ nuclei in compounds **2** and **5** (see Table 4) do not fit with the above-mentioned relationships between $\delta^{13}C(7)$ and the Hammett constants, apparently, for the same reasons for which the charges q_7 in benzyl halides **2** and **5** are inconsistent with the dependences of q_7 on σ_p.

For benzyl halides **1**, **3**, and **4**, no correlations between $\Delta E = E_{LUMO} - E_{HOMO}$ (see Tables 1—3) and the electronic properties of substituents (Hammett constants σ[21]) or the chemical shifts $\delta^{13}C(7)$ (see Table 4) are observed. However, for compounds **1**, there is a pronounced linear dependence ($r = 0.969$) of $\Delta\delta C(7)$ on $1/R_B^3$, where R_B is the volume of Bader's atomic basin of the C(7) atom over which the electron density assigned to this atom[18,19] is integrated. The slope of the dependence of $\Delta\delta C(7)$ on R_B^{-3} is 375 ppm (au)$^{-3}$. This is indicative of the substantial effect of the size of the orbital on the paramagnetic shielding of $^{13}C(7)$ nuclei. The occurrence of the above-mentioned correlation indicates[45,47] that the change in the chemical shift of the C(7) atom in the series of compounds **1a**—**g** is caused by the change in the charge on this atom. Therefore, the change in the chemical shift ($\Delta\delta C(7) = \delta^{13}C(7) - \delta^{13}C(7)^0$), for *para*-substituted benzyl chloride **1**, which contains the X substituent ($\delta^{13}C(7)$), relative to the chemical shift for unsubstituted benzyl chloride **1c** ($\delta^{13}C(7)^0$), correlates rather well ($r = 0.857$ (Bader), 0.937 (NBO), 0.896 (Mulliken), 0.870 (MNDO), and 0.922 (PM3)) with the corresponding changes in the charge $\Delta q_7 = q_7 - q_7^0$ determined from the charges q_7 calculated by different methods. These correlations are described by Eq. (2):

$$\Delta\delta C(7) = a\Delta q_7 + b. \quad (2)$$

The slopes a of the lines described by this equation characterize the sensitivity of a change in the chemical shift to a change in the charge. The average value of a, which was obtained from the results of calculations by five methods, is 58 ppm e^{-1}. This value agrees well with the slope of ~60 ppm e^{-1}, which characterizes the dependence of the chemical shift $\delta^{13}C(7)$ on the charge of the methyl groups bonded to the centers of carbonium ions.[45]

Relationships analogous to the correlation between $\Delta\delta C(7)$ and Δq_7 (Eq. (2)) are also observed for the C(1), H(8), and H(9) atoms in benzyl chlorides **1**. Analogous

dependences are also typical of the C(1), C(7), H(8), and H(9) atoms in benzyl chlorides **3** and benzyl bromides **4**.

The same tendency for a change $\Delta\delta C(7)$ depending on Δq_7 in the case of compounds **1**, **3**, and **4** is a rather strong argument in favor of the fact that in the last two mentioned types of benzyl halides a change in the chemical shift of the C(7) atom is also associated with a change in the electron density on this atom, which, as mentioned above, increases as the electron-withdrawing ability of the X substituent increases.

A detailed analysis of the calculated data on these compounds and the results of topological analysis[18,19] of the electron density in benzyl halides **1** under study gave us an insight into the reasons for the increase in the electron density on the C(7) atom as the electron-withdrawing ability of substituents in benzyl halides increases.

An increase in the electron-withdrawing properties of substituents leads to the expected decrease in the electron density on the C(1) atom of the benzene ring bonded to the benzyl C(7) center. This is evidenced by the positive values of ρ_1 (Eq. (1)) for **1** [0.0164 (Bader), 0.0795 (MNDO)], and **4** [0.0728 (MNDO)] and by the downfield shift of the resonance of the $^{13}C(1)$ nuclei as the value σ_p for the X substituent increases. In this case, the slopes a of the linear dependences of $\Delta\delta C(1)$ on Δq_1 (180 ppm e^{-1} and 144 ppm e^{-1} for **1** and **4**, respectively) agree with the values of the slopes (the commonly accepted value is 160 ppm e^{-1}) of the dependences of $\delta^{13}C$ on the charge in substituted benzenes ($q = 0$) and cyclic and some other ions.[45]

A decrease in the electron density on the C(1) atom in benzyl halides as the electron-withdrawing properties of substituents increase should cause also a decrease in the electron density on the benzyl C(7) center, which is directly bonded to the C(1) atom. However, this decrease should result, in turn, in withdraw of the electron density not only from the H(8) and H(9) atoms bonded to the C(7) atom, but also from the Cl(10) (in compounds **1**—**3**) or from the Br(10) atom (in compounds **4** and **5**) as well.

The decrease in the electron density on the H(8) and H(9) atoms as the electron-withdrawing properties of substituents increase is evidenced by the downfield shift of the resonance of the $^1H(8)$ and $^1H(9)$ nuclei as the Hammett constants s increase (the positive slopes of the linear dependences (Eq. (1)) of q_8 and q_9 on σ). For the above-mentioned hydrogen atoms in benzyl chlorides **1**, the average value (determined from the results of calculations by five methods) of the proportionality coefficient between this shift and the change in the charge is 10.8 ppm e^{-1}, which is close to the proportionality coefficients (10—11 ppm e^{-1}) of the dependences of the chemical shifts of the protons, which are bonded to the positively charged carbon atoms, on the charge.[45]

The analysis of the calculated and experimental data demonstrates that the shift of the electron density from the H(8) and H(9) atoms can compensate only slightly for the decrease in the electron density on the C(7) atom, which is associated with an increase in the electron-withdrawing properties of substituents.

As can be seen from Fig. 2, the electron density on the Cl(10) atom in benzyl chlorides **1** decreases substantially as the electron-withdrawing ability of substituents increases. An analogous situation is also observed in the case of benzyl halides **3** and **4**. Thus, the slopes of the linear dependences (Eq. (1)) of the changes in the charges on the Cl(10) atom in compounds **1**, which were calculated according to Bader and by the MNDO method, are 0.0458 and 0.0278, respectively. According to the results of MNDO calculations, the slopes are 0.0216 and 0.0270 for the Cl(10) and Br(10) atoms in compounds **3** and **4**, respectively. These data and the above-mentioned analogous data obtained for the C(7) atom indicate that the decrease in the electron density on the benzyl Cl(10) atom in compounds **1** (**3**) is 1.5 (1.6) times as large as the increase in the electron density on the benzyl C(7) atom. In benzyl bromides **4**, the decrease in the electron density on the Br(10) atom is 1.1 times as large as the increase in the density on the C(7) atom. This decrease in the electron density on the Cl(10) and Br(10) atoms is sufficiently large that it not only compensates for a decrease in the electron density on the C(7) atom, which is caused by an increase in the electron-withdrawing ability of substituents, but leads to an increase in the density on the last-mentioned atom as well.

Therefore, the shift of the electron density to the benzyl C(7) center from the adjacent halogen atom is the major cause of the increase in the electron density on the C(7) atom in benzyl halides as the electron-withdrawing ability of substituents in the benzene ring increases. An increase in the electron density on the C_α atom as the electron-withdrawing properties of substituents increase is also observed for substituted styrenes, aromatic carbonyl compounds,[43] aromatic carboxylic acids,[43,47,48] and their derivatives.[43] This increase is associated with the shift of the π-electron density to the C_α atom due to polarization of the carbon—carbon or carbon—oxygen π-bond. An increase in the negative charge on the C_α atom in the above-mentioned systems leads to the upfield shift of the resonance of the $^{13}C_\alpha$ nuclei.[43]

For benzyl chlorides **1**, we have carried out topological analysis[18,19] of the electron density distribution, which was described by wave functions with the 6-31G basis set, and demonstrated that an increase in the shift of the electron density from the Cl(10) atom to the C(7) atom as the electron-withdrawing properties of the X substituent increase leads to a linear ($r = 0.989$) increase in the electron density ρ_c at the critical point (3; −1)[18,19] on the C(7)—Cl(10) bond line. Thus, for compounds **1a**—**g**, the values of ρ_c are 0.1224, 0.1233, 0.1247, 0.1252, 0.1259, 0.1276, and 0.1286 e $(au)^{-3}$, respectively. In going from **1g** to **2**, the value of ρ_c becomes even higher (0.1322 e $(au)^{-3}$). The above-

mentioned changes in the electron density along the C(7)—Cl(10) bond line are also evidenced by the Laplacian $\nabla^2\rho_c$, *i.e.*, the second derivative of the distribution function ρ at the critical point.[18,19] The linear (r = 0.986) increase in the negative values of $\nabla^2\rho_c$ (−0.0272 (**1a**), −0.0294 (**1b**), −0.0334 (**1c**), −0.0338 (**1d**), −0.0356 (**1e**), −0.0396 (**1f**), and −0.0420 e (au)$^{-5}$ (**1g**)) as σ_p in benzyl chlorides **1** increases confirms[18,19] the increase in the electron density along the C(7)—Cl(10) bond line as the electron-withdrawing properties of substituents in these compounds increase.

A decrease in the distance R_{Cl} from the critical point to the Cl(10) atom is accompanied by an increase in ρ_c at the critical point along the C(7)—Cl(10) bond line. In the series of compounds **1a—g**, this distance is 2.0650, 2.0602, 2.0530, 2.0486, 2.0438, 2.0333, and 2.0260 au, respectively. In this case, the dependence of R_{Cl} on σ_p is linear (r = 0.995). In benzyl chloride **2**, R_{Cl} is 2.0008 au, while the distance R_7 to the C(7) atom remains virtually unchanged (1.5394±0.0010 au). As a result, the sum of R_{Cl} and R_7 decreases, which is equivalent to a shortening of the C(7)—Cl(10) bond (see Table 1), as the electron-withdrawing ability of substituents increases in the series of compounds **1a—g** and **2**. Therefore, an increase in the electron density ρ_c at the critical point between the C(7) and Cl(10) atoms is equivalent to a decrease in the bond length d between these atoms. The shortening of the C(7)—Cl(10) bond in the series of compounds **1a—g** and **2** is also evidenced by the increase in the order n of this bond (see Table 1).

A shortening of the C(7)—Cl(10) bond and an increase in its order in the series of compounds **1a—g** and **2** are also predicted by the semiempirical MNDO and PM3 methods (see Table 1). According to the results of these calculations, tendencies for a decrease in the lengths of the C(7)—Cl(10) and C(7)—Br(10) bonds and an increase in their orders as the electron-withdrawing properties of substituents increase are also observed in *meta*-substituted benzyl chlorides **3** (see Table 2) and in benzyl bromides **4a—h** and **5** (see Table 3).

In compounds **1a—g**, the electron density at the critical point (3; −1) along the C(1)—C(7) bond line is 0.2498, 0.2489, 0.2477, 0.2488, 0.2485, 0.2481, and 0.2480 e (au)$^{-3}$, respectively, *i.e.*, it decreases regularly as the constant σ_p of the substituent increases. In benzyl chloride **2**, the electron density ρ_c along the C(1)—C(7) bond line is even lower (0.2467 e (au)$^{-3}$). The decrease in the electron density along this bond line in benzyl chlorides **1** is also evidenced by the decrease in the negative values of the Laplacian at the critical point of this bond. For compounds **1a—g**, these values are −0.5196, −0.5168, −0.5120, −0.5151, −05148, −0.5134, and −0.5128 e (au)$^{-5}$, respectively. In the series of these compounds, the distance R_7 between the critical point along the C(1)—C(7) bond line and the benzyl C(7) center decreases linearly (r = 0.931; 1.4451, 1.4475, 1.4481, 1.4385, 1.4370, 1.4325, and 1.4270 au, respectively), whereas the distance R_1 to the C(1) atom on this bond line increases linearly (r = 0.992; 1.3646, 1.3667, 1.3718, 1.3777, 1.3807, 1.3885, and 1.3958 au, respectively) as the value of σ_p increases. In benzyl chloride **2**, R_1 = 1.4525 au. In other words, the critical point on the C(1)—C(7) bond line in benzyl chlorides **1** and **2** shifts to the C(7) atom, whose electronegativity decreases compared to the electronegativity of the C(1) atom as the electron-withdrawing ability of substituents increases.

The changes in the values of R_1 and R_7 result in the increase in their sum from 2.8097 au in **1a** to 2.8228 au in nitrobenzyl halides **1g**. Therefore, the changes in the values of ρ_c, R_1, and R_7 along the C(1)—C(7) bond line are indicative of an elongation of this bond in going from **1a** to **1g**. This is in complete agreement with the data on the increase in the length of the C(1)—C(7) bond and the decrease in its order in the series of compounds **1a—g** (see Table 1). The data in Table 1 demonstrate that in going from **1g** to **2**, the order of the bond under consideration is also decreased.

Pronounced tendencies for an increase in the C(1)—C(7) bond length and a decrease in its order as the electron-withdrawing ability of substituents increases are also observed in *meta*-substituted benzyl chlorides **3** (see Table 2) and benzyl bromides **4a—h** and **5** (see Table 3).

Therefore, an increase in the electron-withdrawing properties of substituents in all benzyl halides studied leads, on the one hand, to an elongation of the C(1)—C(7) bond and a decrease in its order, and on the other hand, to a shortening of the C(7)—Cl(10) or C(7)—Br(10) bond and an increase in its order. To put it differently, *the alternation of the C(1)—C(7) and C(7)—Cl(10) [or C(7)—Br(10)] bond lengths increases as the electron-withdrawing ability of substituents in the benzene rings of benzyl halides increases.*

The obtained data on the shifts of the electron density to the benzyl carbon atom from the adjacent halogen atom as the electron-withdrawing ability of substituents increases allowed us to reveal the cause, which was unclear previously, of the upfield shift of the resonance of the $^{13}C(7)$ nuclei as the electron-withdrawing properties of substituents in benzyl fluorides and benzyl chlorides increase.[43,44] Therefore, the electron density on the C(7) atom increases as the electron-withdrawing ability of substituents increases not only in the case of substituted benzyl chlorides and benzyl bromides, but in benzyl fluorides as well.

The larger length and the smaller order of the C(7)—Hal bond in benzyl halide, which contains an electron-donor substituent (for example, the MeO group), compared to those in benzyl halide, which contains an electron-withdrawing substituent, indicate that the energy of heterolytic cleavage of the C(7)—Hal bond in the former compound is lower than that in the latter. This fact, along with stabilization of the carbonium ion[1,2,49] that formed upon solvolysis, should promote ionization of the C(7)—Hal bond in benzyl halides that contain electron-donor substituents. Finally, an increase

in the negative charge on the benzyl halogen atom as the electron-donating ability of substituents increases should lead to an increase in solvation of this atom by proton-donor solvents and to an increase in the tendency of benzyl halides to undergo ionization at the C(7)—Hal bond. Therefore, the data obtained make it possible to reveal additional factors favorable to an increase in ionization of benzyl halides and in the tendency of these compounds to undergo solvolysis and S_N1 reactions as the donor properties of substituents increase.[49]

According to the data obtained in this work, *stronger electron-withdrawing substituents in the benzene ring are favorable for a decrease in the positive charge on the benzyl carbon atom.* As a consequence, a decrease, rather than an increase,[7] in the reactivity of a nucleophile toward this center should be observed as the electron-withdrawing ability of substituents in benzyl halides increases. An increase in the electron density on the benzyl carbon atom as the electron-withdrawing properties of substituents in benzyl halides increase is equivalent to a decrease in the hardness[50] of the C(7) reaction center. A decrease in the hardness of this center may lead, under certain conditions, to an increase in the regioselectivity of benzylation at the softer reaction center of ambident nucleophiles.[51] Apparently, this is one of the reasons for the increase in regioselectivity of benzylation at the softer allenyl center of the lithium salt of 1,3,3-triphenylpropyne in the series of benzyl halides **1a** < **1b** < **1c** < **1e** < **2**.[8]

The substantial decrease in the energy of LUMO as the electron-withdrawing properties of substituents in benzyl halides increase (see Tables 1—3) should result in an increase in the tendency of these compounds to accept an electron on LUMO. This is in good agreement with the data on the reduction potentials of benzyl halides[52,53] and an increase in their tendency to undergo electron-transfer reactions[54,55] as the electron-withdrawing properties of substituents increase.

We thank Prof. M. W. Schmidt (Iowa State University, Ames, Iowa, USA) for supplying the GAMESS program, Prof. R. F. W. Bader (McMaster University, Hamilton, Ontario, Canada) for supplying the AIMPAC program package, and Prof. H. Bohe (Phillips University, Marburg, Germany) for providing samples of a number of benzyl halides.

This work was supported by the Russian Foundation for Basic Research (Project No. 94-03-09266).

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Received September 11, 1996;
in revised form April 28, 1997