^{35}Cl NQR of the N-Cl Bond and the Modified Townes-Daily Theory *

G. V. Dolgushin, I. M. Lazarev, P. A. Nikitin, and L. I. Larina

Irkutsk Institute of Organic Chemistry, Siberian Division, Academy of Sciences of Russia, 1 Favorsky St., 664033 Irkutsk, Russia

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The modified Townes-Daily equation is shown to be better than the original one for frequencies of compounds having N-Cl bonds. Of the three semi-empirical methods AM 1, MNDO, PM 3, the first is preferable. The asymmetry parameters for the same compounds have been evaluated. The ^{35}Cl NQR frequencies of two tautomers of N-chlorobenzotriazole are compared.

Key words: Nuclear quadrupole resonance; Modified Townes-Daily equation; N-Cl bond; Tautomers of N-chlorobenzotriazole.

A systematic NQR study of substituent effects and nitrogen hybridization on the N-Cl bond is still missing. The scatter of ^{35}Cl NQR data on the N-Cl bond, errors in the assignment of frequencies and the absence of any relationship for the prediction of ^{35}Cl NQR frequencies [1–15] have inspired us to perform this investigation.

The ^{35}Cl NQR frequencies of chloroketemines R′R″C=N-Cl correlate with the sum of the inductive constants ($\Sigma\sigma^*$ [16]) of substituents R′ and R″: $\nu = (43.466 \pm 0.197) + (0.990 \pm 0.055)\,\Sigma\sigma^*$, $r = 0.994$, $s = 0.299$, $n = 6$ (Figure 1). Thus, it turns out that the N-Cl bond ionicity of compounds of this series is sensitive to the effect of substituents at the carbon atom of the azomethyne fragment.

In order to establish general rules for the change in the N-Cl bond, semi-empirical quantum-chemical calculations (AM 1 [17], MNDO [18], PM 3 [19]) with total optimization of the geometry of a series of molecules have been made (Table 1). Based on these calculations, the theoretical ^{35}Cl NQR frequencies ($\nu_{\text{T.-D.}}$) were evaluated using the Townes-Daily approximation. They correlate with the experimental values (ν_{exp}) as follows:

$$\nu_{\text{exp.}} = (-3.530 \pm 3.658) + (1.004 \pm 0.068)\,\nu_{\text{T.-D.}},$$
$$r = 0.967, \quad s = 1.280, \quad \text{(AM 1)}, \qquad (1)$$

$$\nu_{\text{exp.}} = (-2.776 \pm 4.547) + (0.738 \pm 0.089)\,\nu_{\text{T.-D.}},$$
$$r = 0.950, \quad s = 1.584, \quad \text{(MNDO)}, \qquad (2)$$

$$\nu_{\text{exp.}} = (-22.269 \pm 7.972) + (1.296 \pm 0.142)\,\nu_{\text{T.-D.}},$$
$$r = 0.920, \quad s = 1.971, \quad \text{(PM 3)}. \qquad (3)$$

Analysis of these equations shows that the experimental ^{35}Cl NQR frequencies for the N-Cl bond can fairly well be predicted by the AM 1 method, worse by the MNDO method and worst by the PM 3 method. In [20] we have suggested a modified equation in which the diffuse nature of the indicator atom *p*-orbitals is taken into account:

$$\nu = k\left((\xi_z)^3 P_{zz} - \frac{(\xi_x)^3 P_{xx} + (\xi_y)^3 P_{yy}}{2}\right),$$

where ξ_μ is an exponent for the AO of the Slater type and P_{xx}, P_{yy} and P_{zz} are the orbital populations of the

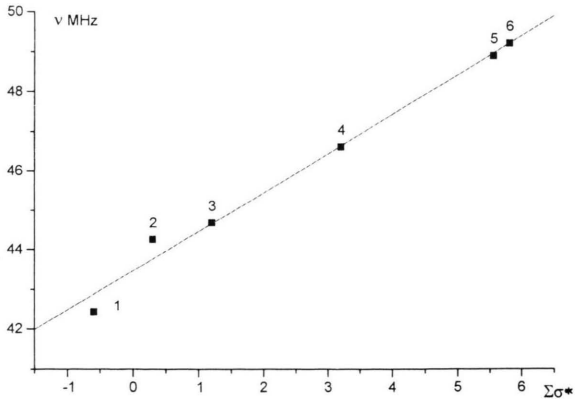

Fig. 1. Correlation between the ^{35}Cl NQR frequencies of chloroketemines R′R″C=N-Cl [1, 2] and the sum of the inductive constants ($\Sigma\sigma^*$) [16] of substituents R′ and R″. R′, R″ = $(CH_3)_3C$, $(CH_3)_3C$ **1**; $(CH_3)_3C$, C_6H_5 **2**; C_6H_5, C_6H_5 **3**; C_6H_5, CF_3 **4**; Cl, CCl_3 **5**; Cl, Cl **6**.

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Reprint requests to Dr. G. V. Dolgushin.

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Table 1. Experimental ($\nu_{exp.}$) [1 – 10] and calculated ^{35}Cl NQR frequencies of compounds having an N-Cl bond, the latter by the Townes-Daily equation ($\nu_{T.-D.}$) and the modified equation ($\nu_{M.T.-D.}$).

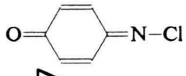
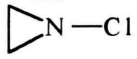
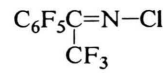
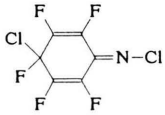
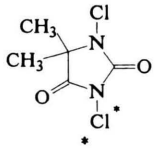
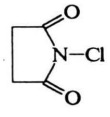
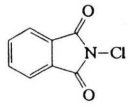
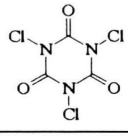
N	Compound	$\nu_{exp.}$ (MHz)	AM 1		MNDO		PM 3	
			$\nu_{T.-D.}$	$\nu_{M.T.-D.}$	$\nu_{T.-D.}$	$\nu_{M.T.-D.}$	$\nu_{T.-D.}$	$\nu_{M.T.-D.}$
1	$[(CH_3)_3C]_2C{=}N\text{-}Cl$	42.433	47.412	44.287	45.489	44.231	51.760	46.302
2	$(CH_3)_2N\text{-}Cl$	43.705	48.674	47.435	47.244	47.025	50.584	47.259
3	$(C_6H_5)_2C{=}N\text{-}Cl$	44.681	48.402	45.544	45.372	44.088	52.684	47.476
4		44.992	48.713	46.123	46.040	45.066	52.732	47.850
5		45.604	48.794	47.094	46.709	46.195	52.794	49.103
6		46.616	50.332	48.133	47.961	47.365	54.664	50.524
7		49.123	51.056	48.932	49.205	48.877	55.644	51.130
8	$Cl_2C{=}N\text{-}Cl$	49.205	51.321	49.318	49.837	49.528	54.979	50.725
9	$C_6F_5NCl_2$	51.180	51.979	52.135	49.911	50.792	56.199	54.750
10	$ClCH_2CH_2CONHCl$	51.359	54.125	53.728	50.094	50.529	53.555	51.255
11		53.005	57.947	58.047	55.109	55.501	59.358	57.294
12	$CCl_3CONHCl$	53.520	56.331	56.391	50.890	51.515	55.150	53.440
13		53.639	55.073	55.014	53.642	54.475	57.601	55.493
	*	55.960	59.512	59.931	57.154	58.113	60.356	58.706
14		54.088	58.833	58.769	56.139	56.574	60.274	58.056
15		55.424	58.920	58.706	56.046	56.292	59.934	57.538
16		58.902	62.092	63.850	59.282	61.096	62.032	61.685

Table 2. The parameters of the correlation equation of $\nu_{exp.} = A + B\,\nu_{calc.}$ for N-chlorobenzotriazole tautomers ($n = 18$).

Compound	Method	Equation	A	B	r	S
1-chlorobenzotriazole	AM 1	T.-D.	-4.786 ± 4.351	1.032 ± 0.081	0.954	1.534
		M.T.-D.	7.457 ± 3.056	0.817 ± 0.058	0.962	1.392
2-chlorobenzotriazole		T.-D.	-1.814 ± 3.451	-1.814 ± 3.451	0.967	1.302
		M.T.-D.	10.021 ± 2.538	0.8763 ± 0.047	0.970	1.238
1-chlorobenzotriazole	MNDO	T.-D.	-4.092 ± 5.000	1.069 ± 0.098	0.939	1.757
		M.T.-D.	-3.055 ± 3.833	0.928 ± 0.074	0.952	1.569
2-chlorobenzotriazole		T.-D.	-2.690 ± 4.187	1.038 ± 0.081	0.954	1.533
		M.T.-D.	4.158 ± 3.144	0.903 ± 0.061	0.966	1.335
1-chlorobenzotriazole	PM 3	T.-D.	-24.292 ± 8.156	1.336 ± 0.145	0.917	2.046
		M.T.-D.	-4.196 ± 4.134	1.032 ± 0.078	0.958	1.478
2-chlorobenzotriazole		T.-D.	-21.387 ± 7.254	1.280 ± 0.129	0.928	1.915
		M.T.-D.	-2.040 ± 3.551	0.987 ± 0.066	0.966	1.332

Table 3. The difference $\Delta\nu = \nu_{exp.} - \nu_{calç}$ between the experimental NQR frequencies ($\nu_{exp.}$) and those calculated $\nu_{calc.}$ by (1–6) for the assumed N-chlorobenzotriazole tautomers.

Compound	AM 1		MNDO		PM 3	
	$\Delta\nu_{T.-D.}$	$\Delta\nu_{M.T.-D.}$	$\Delta\nu_{T.-D.}$	$\Delta\nu_{M.T.-D.}$	$\Delta\nu_{T.-D.}$	$\Delta\nu_{M.T.-D.}$
1-chlorobenzotriazole	−3.776	−3.312	−3.576	−3.433	−3.086	−2.836
2-chlorobenzotriazole	1.774	2.136	0.105	0.007	0.689	0.986

diagonal population-bond order sub-matrix of the chlorine atom *p*-electrons.

Making use of this equation, we calculated the frequencies $\nu_{M.T.-D.}$ for the compounds presented in Table 1 and compared them with the experimental values:

$$\nu_{exp.} = (8.421 \pm 2.618) + (0.795 \pm 0.050)\,\nu_{M.T.-D.},$$
$$r = 0.972, \quad s = 1.181, \quad \text{(AM 1)}, \qquad (4)$$

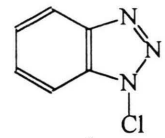
$$\nu_{exp.} = (4.153 \pm 3.401) + (0.903 \pm 0.066)\,\nu_{M.T.-D.},$$
$$r = 0.962, \quad s = 1.379, \quad \text{(MNDO)}, \qquad (5)$$

$$\nu_{exp.} = (-2.907 \pm 3.849) + (1.005 \pm 0.073)\,\nu_{M.T.-D.},$$
$$r = 0.963, \quad s = 1.357, \quad \text{(PM 3)}. \qquad (6)$$

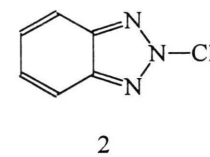
One can see a marked improvement in the correlation characteristics of the equations and a leveling out of the capability of predicting frequencies of the three methods.

Non-empirical calculations of the ^{35}Cl nuclear quadrupole coupling constant have been reported for N-chloraziridine [21]. Semi-empirical NQCC calculations for this compound are slightly less predictive than non-empirical procedures.

It has also been reported [5] that for 1-chlorobenzotriazole the BEEM-π (bond electronegativity equalization method [22]) calculation, fairly effective in predicting NQR frequencies, induces serious disagreements with the experiment. Probably in this case it should be taken into consideration that N-chlorobenzotriazole can exist as two tautomers:



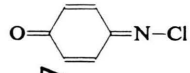
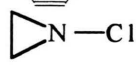
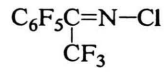
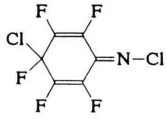
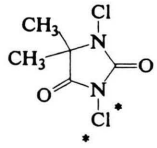
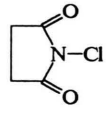
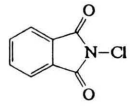
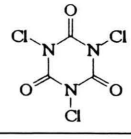
1



2

As neither the method of synthesis, nor structural data are presented in [5], it is quite possible that the spectrum presented in [5] is that of 2-chlorobenzotriazole. We have carried out quantum chemical calculations for the two tautomers. Introduction of the data obtained for tautomer 1 into the correlation equations (1–6) leads to deterioration of the correlation parameters (Table 2). For tautomer **2** a decrease in dispersion and an increase of the correlation coefficient were observed nearly in all cases. The correlation obtained in

Table 4. Calculated asymmetry parameters of the EFG (%) of N-Cl-bond-containing compounds.

N	Compound	AM 1		MNDO		PM 3	
		$\eta_{T.-D.}$	$\eta_{M.T.-D.}$	$\eta_{T.-D.}$	$\eta_{M.T.-D.}$	$\eta_{T.-D.}$	$\eta_{M.T.-D.}$
1	$[(CH_3)_3C]_2C{=}N\text{-}Cl$	3.43	2.99	3.54	2.13	3.40	1.97
2	$(CH_3)_2N\text{-}Cl$	0.12	0.43	0.18	0.78	0.26	0.60
3	$(C_6H_5)_2C{=}N\text{-}Cl$	3.49	3.16	4.23	3.32	4.25	3.83
4		4.30	4.22	5.44	5.01	5.40	5.45
5		0.31	0.16	0.36	0.75	0.64	0.24
6		4.52	4.47	5.20	4.65	5.31	5.52
7		5.60	5.51	6.40	5.88	7.44	7.92
8	$Cl_2C{=}N\text{-}Cl$	3.54	3.23	3.88	2.91	4.52	4.43
9	$C_6F_5NCl_2$	1.69	1.62	1.65	1.07	0.75	0.14
10	$ClCH_2CH_2CONHCl$	0.36	0.12	0.57	0.14	0.51	0.47
11		0.37	0.34	0.63	0.36	0.30	0.16
12	$CCl_3CONHCl$	0.54	0.09	0.63	0.01	0.38	0.40
13		0.44	0.01	0.54	0.47	0.73	0.08
	*	0.51	0.30	0.85	0.31	0.46	0.10
14		0.45	0.29	0.71	0.23	0.46	0.15
15		0.52	0.34	0.88	0.35	0.54	0.20
16		0.60	0.50	1.18	0.85	0.51	0.32

the case of AM 1 by the modified Townes-Daily equation is the only exception. Furthermore, we introduced the calculated NQR frequencies of the two tautomers into (1–6) and found a difference from the experimental value of 56.743 MHz (Table 3).

On the basis stated above, the 56.743 MHz signal is suggested to correspond to 2-chlorobenzotriazole. We also suppose that in N-chlorobenzotriazole crystals there are no strong intermolecular interactions.

In many works devoted to NQR studies of the electronic effects in molecules having N-Cl bonds, the asymmetry parameter is either taken to be equal to zero or ignored. Nevertheless, based on BEEM-π calculations [5], this parameter can be high for some compounds (for example, 15.7% for compound **4** (Table 1). Our calculations imply that these data should be taken into account (Table 4).

As seen from Table 4, non-zero values should be expected for compounds possessing a >C=N-Cl fragment. These values grow with strengthening of the electron-withdrawing properties of substituents at the carbon atom. In this case the η parameters obtained by the Townes-Daily theory do not differ much from those calculated by the modified equation and are considerably lower than those predicted by the BEEM-π method. Earlier we have reported the experimental parameters to be three times those predicted from MNDO calculations in the Townes-Daily approximation [23]. Seemingly, this conclusion can be extended to other semi-empirical methods. Unfortunately, our conclusions cannot be checked at present due to the absence of experimental data.

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