Theoret. Chim. Acta (Berl.) 34, 137—144 (1974)

INDO Investigation of the Halogen N.Q.R. Frequencies and ^{14}N Nuclear Quadrupole Coupling Constants of Halothiophenes and Halopyridines

V. Galasso
Istituto di Chimica, Università di Trieste, Trieste, Italy

Received February 11, 1974

The ^{35}Cl, ^{79}Br, and ^{127}I N.Q.R. frequencies of a number of halothiophenes and halopyridines and the ^{14}N nuclear quadrupole coupling constants of halopyridines have been determined in terms of the Kaplansky-Whitehead theory with the INDO MO approximations using a consistent set of atomic parameters derived from SCF Hartree-Fock calculations. The theoretical spectral properties are in satisfactory overall agreement with experiment. This result supports the validity of using the above method to provide reliable predictions of N.Q.R. parameters for heteroaromatic systems.

Key words: N.Q.R. parameters – Halothiophenes – Halopyridines

1. Introduction

In view of the growing interest in the N.Q.R. spectra of aza- and thioaromatic systems containing halogens (^{35}Cl, ^{79}Br, and ^{127}I) [1] it would be desirable to have reasonable theoretical predictions both to assist in the experimental analysis and to compare with specific experimental results when these are available.

The semiempirical all-valence-electron INDO SCF-MO method [2] has been extensively and successfully used for the calculation of important magnetic resonance properties of a variety of heteroaromatic molecules and radicals. In particular, it has been shown that this method is capable of providing satisfactory predictions of nuclear spin coupling constants [3], ^{13}C chemical shifts [4] and hyperfine coupling constants [5]. It is therefore of great interest to examine the suitability of the standard INDO method to reproduce satisfactorily also the N.Q.R. parameters of heteroaromatic compounds. In order to obtain a reasonable conclusion, the test has been performed taking into account all the halothiophenes, all the monohalopyridines and some symmetric dihalopyridines, for which sufficient experimental data are available for comparison.

The halogen N.Q.R. frequencies and the ^{14}N nuclear quadrupole coupling constants of these compounds have been evaluated and compared with observation. The theoretical predictions of halogen and nitrogen asymmetry parameters have been also analyzed.

2. Method

2.1. INDO *Parameters*

The standard INDO method has been adopted. However, the incompleteness of the spectroscopic data for the heavy atoms renders the "semiempirical" determination of their core matrix elements impossible. In order to preserve the internal consistency in the calculations all the required parametrization has therefore been chosen independent of experimental quantities in line with the suggestion by Deb and Coulson [6]. In particular, the orbital electronegativities $\frac{1}{2}(I+A)$ of the valence *s* and *p* electrons have been evaluated from the average energies of appropriate atomic configurations ($s^m p^n$, $s^{m-1}p^{n+1}$, $s^m p^{n+1}$, $s^m p^{n-1}$, and $s^{m-1}p^n$) obtained from Hartree-Fock SCF calculations [6–8]. As to the Slater-Condon parameters F^2 and G^1: a) the theoretical values reported by Deb and Coulson [6] have been adopted for the halogen atoms; b) the F^2 integrals of C, N, O, and S and the G^1 integrals of N and O have been obtained on the basis of the least-squares procedure suggested by Slater [9]; c) the G^1 integral of C has been estimated by quadratic extrapolation from the values of F, O, and N, while that of S has been given the theoretical value determined by Watson and Freeman [10]. The F^0 integrals have been obtained from the following formulas (in a.u.) derived for Slater-type atomic orbitals with integer principal quantum number:

$$F^0(2s,2s)=(93/256)\,\zeta\,,\qquad F^0(3s,3s)=(793/3072)\,\zeta\,,$$

$$F^0(4s,4s)=(26333/131072)\,\zeta\,,\qquad F^0(5s,5s)=(43191/262144)\,\zeta\,.$$

The orbital exponents ζ have been chosen as the arithmetic mean of the ζ_s and ζ_p values given by Clementi and Raimondi [11].

The bonding parameters β^0_{A} adopted for the first-row elements are those recommended by Pople and Segal [12], while those for the non first-row atoms (X) have been determined from those of the corresponding first-row atoms (Y) using the recursion formula proposed by Santry and Segal [13]:

$$\beta^0_{\mathrm{X}}=\beta^0_{\mathrm{Y}}(U^{\mathrm{X}}_{ns}+U^{\mathrm{X}}_{np})/(U^{\mathrm{Y}}_{2s}+U^{\mathrm{Y}}_{2p})\,,$$

where the *U* quantities are the appropriate local core matrix elements.

The full INDO parametrization adopted in the present calculations[1] is collected in Table 1. (The *s*-orbital electronegativity and β^0_{A} of hydrogen have been taken from Pople and Segal [14].)

2.2. N.Q.R. *Frequencies and Constants*

The halogen N.Q.R. frequencies have been determined using the procedure of Kaplansky and Whitehead [15]. From the density matrix a 3 × 3 submatrix for the halogen with elements $p_{ij}(i, j=x, y,$ or $z)$ is diagonalized to give the *p*-orbital populations P_{xx}, P_{yy}, and P_{zz} from which the principal components of the quadrupole coupling tensor q_{xx}, q_{yy}, and q_{zz} and the asymmetry parameter η are calculated:

$$q_{xx}=[P_{xx}-\tfrac{1}{2}(P_{yy}+P_{zz})]\,C_0\,,$$

---

[1] For discussion on the validity of the adopted parameterisation scheme see Ref. [6].

Table 1. INDO parameters in units of eV ≈ 0.160 192 aJ

Atom	ζ	$\frac{1}{2}(I+A)_s$	$\frac{1}{2}(I+A)_p$	F^0	F^2	G^1	$-\beta_A^0$
H	1.2000	7.176		20.4075			9
C	1.5881	13.150	4.776	15.6982	6.3700	9.3733	21
N	1.9203	18.642	6.065	18.9819	7.8394	11.0039	25
O	2.2362	25.142	7.548	22.1046	9.0277	12.7306	31
F	2.5569	32.650	9.251	25.2742	10.3634	14.5536	39
S	1.9748	17.600	6.159	13.8708	5.9301	8.5173	19.76
Cl	2.1974	22.889	7.637	15.4344	6.6843	9.4913	24.17
Br	2.4476	21.367	7.108	13.3801	6.0446	8.4035	21.23
I	2.5015	17.704	6.423	11.2145	5.2354	7.1057	17.81

and similarly for q_{yy} and q_{zz}, and

$$\eta = |q_{xx} - q_{yy}|/|q_{zz}| ,$$

where C_0 is the quadrupole coupling constant for valence shell p-electron. This is taken to have the values 109.746, −769.756, and 2292.172 MHz for ^{35}Cl, ^{79}Br, and ^{127}I respectively [16]. The N.Q.R. frequencies have been calculated using the relations [17]:

$$\nu = (q_{zz}/2)\,(1+\eta^2/3)^{\frac{1}{2}} \qquad \text{for } ^{35}\text{Cl and } ^{79}\text{Br, and}$$

$$\nu_1 = (q_{zz}3/20)\,(1+\eta^2 5/54)$$

$$\nu_2 = (q_{zz}3/10)\,(1-\eta^2 11/54) \quad \text{for } ^{127}\text{I}.$$

The nuclear quadrupole coupling constant q_{xx} of ^{14}N in the halopyridines has been evaluated adopting for the nuclear quadrupole coupling constant of an electron in a valence $2p$ orbital of ^{14}N the best value (−9.1 MHz) obtained from multiple zeta calculations [18].

2.3. Geometry

Since structural data are lacking, idealized structures have been formed by connecting the actual geometries of thiophene and pyridine (as derived from microwave investigations [19]) with standard carbon-halogen bonds: C–Cl 0.170 nm, C–Br 0.185 nm, and C–I 0.205 nm.

3. Results and Discussion

The theoretical and experimental [20–26] N.Q.R. frequencies of ^{35}Cl, ^{79}Br, and ^{127}I in halothiophenes and halopyridines are reported in Tables 2–5, where the given entries for the α or β atoms in the trihaloderivatives are the average of the two individual values. The ^{14}N nuclear quadrupole coupling constants of halopyridines are collected in Table 6, where the "experimental" data on bromoderivatives (see note below the table) are reported only for the sake of completeness.

3.1. Halothiophenes

The N.Q.R. frequency of α-bromine higher than β-bromine and the increase of the resonance frequency with increasing number of Br atoms on the ring are general features observed for bromothiophenes (Table 2) well reproduced by the present INDO results. Indeed, both the calculated ν_α and ν_β increase with the number of Br atoms and ν_α is always found to be greater than ν_β except in the case of 2, 3, 4- and 2, 3, 4, 5-bromothiophene. Furthermore, the calculation reflects fairly well the observed trends: there is only one discrepancy for ν_α in the case of the tribromoderivatives. The accuracy of the theoretical values is satisfactory,

Table 2. Calculated[a] and experimental (at 77 °K) [20] ^{79}Br N.Q.R. frequencies (MHz) of bromothiophenes

Compound	ν_α		ν_β		η_α	η_β
	Calc.	Exp.	Calc.	Exp.	(%)	(%)
2-Br	276.37	290.93			4.3	
3-Br			275.40	278.60		4.2
2, 3-Br	280.85		279.30		3.9	4.0
2, 4-Br	278.65		277.19		4.3	4.2
2, 5-Br	278.06	293.27			3.9	
3, 4-Br			280.00	288.86		4.2
2, 3, 4-Br	282.56	297.95	282.59	295.88	4.1	4.1
2, 3, 5-Br	281.13	300.12	281.00	290.43	4.0	4.0
2, 3, 4, 5-Br	283.87	305.73	285.11	296.76	3.8	3.9

[a] ν_α and ν_β refer to α- and β-bromine respectively.

Table 3. Calculated and experimental (at 77 °K) [21] ^{35}Cl N.Q.R. frequencies (MHz) of chlorothiophenes

Compound	ν		η
	Calc.	Exp.	(%)
2-Cl	36.67	36.68[b]	5.4
3-Cl	36.77		5.7
2, 3-Cl[a]	37.28		4.9
	37.36		5.1
2, 4-Cl[a]	36.90		5.7
	36.95		5.7
2, 5-Cl	36.88	37.04[c]	5.0
3, 4-Cl	37.40		5.6
2, 3, 4-Cl[a]	37.48		5.2
	37.77		5.3
2, 3, 5.-Cl[a]	37.29		4.9
	37.54		5.2
2, 3, 4, 5-Cl[a]	37.67	37.52	4.8
	38.14	38.50	5.1

[a] The first entry refers to α-chlorine and the second to β-chlorine.

[b] Frequency of 2-chloro-5-methyl-thiophene.

[c] Average frequency.

Table 4. Calculated and experimental (at 298 °K) [22] ^{127}I N.Q.R. frequencies (MHz) of iodothiophenes

Compound	Calc.		Exp.		η
	ν_1	ν_2	ν_1	ν_2	(%)
2-I	262.44	524.71	293.83[b]	585.98[b]	3.2
3-I	260.14	520.14			3.1
2, 3-I[a]	265.81	531.46			3.2
	262.81	525.48			3.0
2, 4-I[a]	264.69	529.20			3.3
	261.79	523.42			3.1
2, 5-I	263.77	527.25	297.25[c]	592.60[c]	3.1
3, 4-I	263.75	527.36			3.1
2, 3, 4-I[a]	267.59	535.00			3.3
	265.59	531.04			3.0
2, 3, 5-I[a]	266.29	532.43			3.1
	264.32	528.50			3.0
2, 3, 4, 5-I[a]	268.40	536.65	312.00		3.1
	267.33	534.52	298.00		2.9

[a] The first entry refers to α-iodine and the second to β-iodine.

[b] Frequency of 2-iodo-5-carboxy-thiophene.

[c] Average frequency.

Table 5. Calculated and experimental (at 77 °K) [22–24] halogen N.Q.R. frequencies (MHz) of halopyridines

X =	^{35}Cl		η	^{79}Br		η	^{127}I		η
Compound	Calc.	Exp.	(%)	Calc.	Exp.	(%)	Calc.	Exp.	(%)
2-X	34.91	34.19	8.2	261.93	265.21	6.3	247.83 495.33		4.8
3-X	37.15	35.23	6.5	278.42		4.8	263.43 526.66		3.6
4-X	36.22	34.74	8.5	271.92		6.4	257.65 514.93		4.9
2, 6-X	35.06	33.85[a]	8.5	263.75		6.4	249.87 499.40		4.8
3, 5-X	37.28	35.60	6.7	280.06	278.00	5.0	265.11 530.00	279.11 557.64	3.7

[a] At room temperature.

the results being numerically better for ν_β. The somewhat less accurate reproduction of ν_α is likely dependent on the influence of the proximate heteroatom.

The paucity of experimental data on the chlorothiophenes prevents a complete check of the calculated values (Table 3). However, the resonance frequencies evaluated for 2-, 2, 5-, and 2, 3, 4, 5-chlorothiophene are in excellent agreement with observation. From Table 3 it is also seen that the frequencies of both the α- and β-chlorine atoms are expected to behave just as those of the Br atoms in the analogous compounds, i.e. to become higher increasing the halogenation. A singular aspect of the INDO results is that, contrary to current

Table 6. Calculated and experimental (at 77 °K) [25, 26] ^{14}N nuclear coupling constants (MHz) of halopyridines

X=	Cl		Br		I
Compound	Calc.	Exp.	Calc.	Exp.	Calc.
2-X	3.960	4.452	3.992	(4.65)[a]	4.000
3-X	4.090	4.628	4.065	(4.70)[a]	4.052
4-X	3.980	4.562	4.008	(4.70)[a]	4.029
2, 6-X	3.842	4.256	3.903	4.330	3.919
3, 5-X	4.098	4.630	4.049		4.026

[a] Value estimated from the roughly linear relationship between the N.Q.R. coupling constants and the ^{14}N chemical shifts found for pyridines with approximately spherical substituents. See Ref. [26].

thinking [27], the Cl atom in the α-position is predicted to resonate at slightly lower frequency than in the β-position. This result may be an inherent consequence of the approximations assumed in the method or even arise from unsatisfactory nature of the geometrical models. An argument in favour of the latter observation is provided by the results of CNDO/BW calculations on chloroorganic systems [28], which show that slight geometry changes have a significant effect on the ^{35}Cl N.Q.R. frequency. However any conclusion about the consistency of the present theoretical finding must await adequate experimental information.

Also in the case of the iodothiophenes there are few experimental data available for comparison. Although somewhat underestimated, the computed frequencies compare reasonably well with observation on 2-, 2, 5-, and 2, 3, 4, 5-iodothiophene. The theoretical results on the iodothiophenes show the characteristic features observed in the spectra of the bromoderivatives; i.e. the resonance frequencies of both the α- and β-iodine raise with increasing number of I atoms on the ring and the nucleus at the α-site resonates higher than the nucleus at the β-site (Table 4).

3.2. Halopyridines

Inspection of Table 5 shows that the comparison of the theoretical values with the available spectral information is very satisfactory. For all three types of halopyridines the calculated resonance frequencies raise in the order: *ortho* < *para* < *meta*. This behaviour reflects correctly the internal order of the experimental frequencies of the monochloropyridines and is also in line with the parallel variation of ionic character of the carbon-halogen bond. The slight frequency shift with increasing number of halogen atoms on the ring is also accounted for; the apparent discrepancy between theory and observation in the case of 2- and 2, 6-chloropyridine is certainly due to the fact that the relative experimental frequencies refer to different temperatures. Finally, it is noticeable that the resonance frequency of the 2-substituted pyridine is predicted to be lower than of the analogous 2-substituted thiophene in agreement with observation.

One of the characteristic features of ^{14}N quadrupole resonance data is that the asymmetry parameter η is very high. Therefore a satisfactory reproduction of the ^{14}N resonance frequencies requires an accurate knowledge of this parameter. For the nitrogen nucleus in pyridine the present approach yields a value of 9% to be compared with the experimental value of 39% [25]. This failure, however, is not unexpected since the Kaplansky-Whitehead theory takes into account only the "local" contributions to the electric field gradient. On the other hand, also the non-empirical interpretation of ^{14}N nuclear quadrupole data of pyridine has not been particularly successful giving a η of only 11% [29]. Due to this difficulty, we limited ourself to the investigation of the ^{14}N nuclear coupling constants neglecting the resonance frequencies. Both the calculated and experimental constants (Table 6) follow the same trend of the related halogen resonance frequencies: *ortho* < *para* < *meta*. The observed coupling decrease on passing from 2- to 2,6-chloropyridine and the virtual coupling constancy on passing from 3- to 3,5-chloropyridine are well accounted for by the INDO calculations. The computed constants are somewhat underestimated, but it must be noted that the agreement between theory and experiment becomes almost quantitative if a quadrupole coupling constant per *p*-electron of -10.2 MHz is assumed for ^{14}N.

About the halogen asymmetry parameters, these appear to be predicted with the correct order of magnitude for both the halothiophenes and halopyridines. The theoretical values for analogous derivatives of thiophene or pyridine fairly well obey:

$$\eta_{\mathrm{Cl}} : \eta_{\mathrm{Br}} : \eta_{\mathrm{I}} \approx 1 : 0.75 : 0.60 .$$

This finding corroborates the current thinking that despite the more polarizable nature of the halogen atom along the series Cl, Br, and I, a decrease of η is to be expected in view of the increased length of the carbon-halogen bond and the more diffuse nature of the *p*-orbitals. Another point worth mentioning is the prediction of greater η for the halopyridines relative to the halothiophenes:

$$\eta_{\mathrm{pyridine}}/\eta_{\mathrm{thiophene}} \approx 1.4 ,$$

diagnostic of greater double-bond character of the carbon-halogen bond in the halopyridines.

3.3. Conclusion

The halogen N.Q.R. frequencies of a variety of halothiophenes and halopyridines and the ^{14}N nuclear coupling constants of halopyridines have been determined in terms of the Kaplansky-Whitehead theory with the INDO MO approximations. Despite of the inherent limitations of the theory and the approximate nature of the adopted geometries, on the whole the calculation accounts satisfactorily for the general features of the observed spectra. The reproduction of the spectral data is fair: the order of magnitude is always correct and the fit is good especially for the chloroderivatives. Also, the theory provides consistent predictions of halogen asymmetry parameters.

From the body of these findings it can be argued that the Kaplansky-Whitehead theory with the INDO MO approximations is able to provide good predictions of ^{14}N nuclear coupling constants and of halogen N.Q.R. frequencies and asymmetry parameters of heterocyclic compounds. This result seems to be particularly significant in view of the fact that the choice of the atomic parameters required in the INDO method has been made without recourse to any fitting of N.Q.R. data.

This work was carried out with the support of the Consiglio Nazionale delle Ricerche (C.N.R.) of Italy.

References

1. a) Lucken, E. A. C.: Nuclear quadrupole coupling constants, Chapter 10 and 11. New York: Academic Press 1969
   b) Lucken, E. A. C.: In: Katritzky, A. R. (Ed.): Physical methods in heterocyclic chemistry, Vol. 4, Chapter 2. New York: Academic Press 1971
2. Pople, J. A., Beveridge, D. L., Dobosh, P. A.: J. Chem. Phys. **47**, 2026 (1969)
3. See e.g.: Maciel, G. E., McIver, J. W., Jr., Ostlund, N. S., Pople, J. A.: J. Am. Chem. Soc. **92**, 1, 11, 4497 (1970)
   Wasylishen, R., Schaefer, T.: Can. J. Chem. **50**, 2989 (1972); **51**, 961 (1973)
   Galasso, V.: Chem. Phys. Letters **21**, 54 (1973)
4. See e.g.: Galasso, V.: Mol. Phys. **26**, 81 (1973); Org. Magn. Res. (in the press)
5. See e.g.: Pople, J. A., Beveridge, D. L., Dobosh, P. A.: J. Am. Chem. Soc. **90**, 4201 (1968)
   Kasai, P. H., McLeod, D., Jr.: J. Am. Chem. Soc. **95**, 27, 4801 (1973)
   Galasso, V., Trinajstić, N.: J. Chim. Phys. **70**, 1489 (1973)
   Galasso, V.: Org. Magn. Res. **6**, 5 (1974)
6. Deb, B. M., Coulson, C. A.: J. Chem. Soc. A 958 (1971)
7. Roothaan, C. C., Kelly, P. S.: Phys. Rev. **131**, 1177 (1963)
8. Clementi, E.: Tables of atomic functions, supplement to IBM J. Res. Dev. **9**, 2 (1965)
9. Slater, J. C.: Quantum theory of atomic structure, Vol. 1, pp. 343–348. New York: McGraw-Hill 1960
10. Watson, R. E., Freeman, A. J.: Phys. Rev. **123**, 521 (1961)
11. Clementi, E., Raimondi, D. L.: J. Chem. Phys. **38**, 2686 (1963)
    Clementi, E., Raimondi, D. L., Reinhardt, W. P.: J. Chem. Phys. **47**, 1300 (1967)
12. Pople, J. A., Segal, G. A.: J. Chem. Phys. **43**, S 136 (1965)
13. Santry, D. P., Segal, G. A.: J. Chem. Phys. **47**, 158 (1967)
14. Pople, J. A., Segal, G. A.: J. Chem. Phys. **44**, 3289 (1966)
15. Kaplansky, M., Whitehead, M. A.: Trans. Faraday Soc. **65**, 641 (1969)
16. Ref. [1a], p. 139
17. Ref. [1a], p. 39
18. O'Konski, C. T., Ha, T. K.: J. Chem. Phys. **56**, 3169 (1972)
19. Bak, B., Hansen-Nygaard, L., Rastrup-Andersen, J.: J. Mol. Spectry. **2**, 361 (1958)
    Bak, B., Christensen, D., Hansen-Nygaard, L., Rastrup-Andersen, J.: J. Mol. Spectry. **7**, 58 (1961)
20. Dormindontov, Yu. P., Grechishkin, V. S., Gushchin, S. I.: Org. Magn. Res. **4**, 599 (1972)
21. Dewar, M. J. S., Lucken, E. A. C.: J. Chem. Soc. 426 (1959)
    Hooper, H. O., Bray, P. J.: J. Chem. Phys. **29**, 444 (1960)
22. Bogaard, M. P.: Thesis, University of Sydney (1967)
23. Segel, S. L., Barnes, R. G., Bray, P. J.: J. Chem. Phys. **25**, 1286 (1956)
24. Bray, P. J., Moskowitz, S., Hooper, H. O., Barnes, R. G., Segel, S. L.: J. Chem. Phys. **28**, 99 (1958)
25. Guibé, L., Lucken, E. A. C.: Mol. Phys. **14**, 79 (1968)
26. Witanowski, M., Saluvere, T., Stefaniak, L., Januszewski, H., Webb, G. A.: Mol. Phys. **23**, 1071 (1972)
27. Ref. [1b], p. 39
28. Cohen, A. J., Whitehead, M. A.: J. C. S. Faraday Trans. II. 649 (1972)
29. Kochanski, E., Lehn, J. M., Levy, B.: Theoret. Chim. Acta (Berl.) **22**, 111 (1971)

Prof. Dr. V. Galasso
Istituto di Chimica
Università di Trieste
I-34127 Trieste, Italy