MINDO/2 Calculations of Nuclear Quadrupole Coupling Constants of the Chlorobenzenes[1]

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Summary MINDO/2 calculations of nuclear quadrupole coupling constants of the chlorobenzenes are reported giving in all cases good agreement with experimental values.

WHILE nuclear quadrupole coupling constants have been calculated successfully by *ab initio* methods for a few simple molecules, the methods used could not be applied to systems large enough to be of interest to organic chemists without prohibitive expense. Equally, attempts to carry out such calculations by more approximate procedures have not as yet proved too successful. Here we describe a promising approach based on a recently developed semiempirical SCF MO treatment (MINDO/2[4]). In this approximation, differential overlap is neglected apart from the one-centre repulsion integrals (ij,ij) and one-electron core resonance integrals. All the valence electrons, σ and π, are included in the calculation, these being assumed to move in a fixed

core composed of the nuclei and inner shell electrons. With these assumptions the LCAO MO expression[5] for q_z^α, the field gradient along the z axis of nucleus α, becomes:

$$q_z^\alpha = \overset{\alpha}{\underset{i}{\Sigma}} P_{ii} q_{ii}^\alpha + \underset{\beta \neq \alpha}{\overset{\beta}{\Sigma}} [\underset{j}{\Sigma} P_{jj} q_{jj}^\alpha + q_{core}^\beta] \tag{1}$$

where i is a valence shell AO of atom α and j of some other atom β, P_{kk} is the electron population in orbital k of atom α or β, q_{core}^β is the contribution to q_z^α by the charge on the core of atom β, and in the usual notation[5]

$$q_{kk}^\alpha = \int \phi_k \frac{(3\cos^2\theta - 1)}{r_{\alpha\beta}^3} \phi_k d\tau \tag{2}$$

Equation (2) can also be derived[6] from the general LCAO MO expression by making the Mulliken-like approximation

$$q_{mn}^\alpha = \tfrac{1}{2} S_{mn}(q_{mm}^\alpha + q_{nn}^\alpha) \tag{3}$$

By analogy with the neglect of penetration integrals in semiempirical SCF MO treatments,[7] we may assume that

$$q_{jj}^\alpha \simeq - q_{core}^\beta / Z^\beta \qquad (4)$$

where the charge on the core of atom β is $Z^\beta e$. Equation (1) then becomes:

$$q_z^\alpha = \sum_i^\alpha P_{ii}^\alpha q_{ii}^\alpha + \sum_\beta \frac{f^\beta q_{core}^\beta}{Z^\beta} \qquad (5)$$

where f^β is the net charge on atom β $(i.e.\ Z^\beta - \sum_j^\beta P_{jj}^\beta)$.

The preliminary studies reported here refer to ^{35}Cl coupling constants in the chlorobenzenes. In order to carry out calculations for these, we needed the MINDO/2 parameters[4] for CCl, HCl, and ClCl interactions. These were determined as before[4] by fitting the heats of formation and bond lengths for a set of standard molecules; full details will be given elsewhere. The parameters used here are listed in Table 1, those for CC, CH, and HH being from ref. 4b.

TABLE 1

Parameters for carbon, hydrogen and chlorine

	C–C	C–H	H–H	C–Cl	Cl–Cl	H–Cl
β	0·3327	0·3356	0·4174	0·3122	0·2757	0·3832
$\alpha(\text{Å}^{-1})$	1·7919	1·2002	0·9319	1·5396	1·5081	0·9694

In the neutral molecules the net charges f^β should be small; since q_{core}^β varies inversely as $1/r^3_{\alpha\beta}$, the contributions of atoms not directly linked to atom α should be negligible. Furthermore our calculations indicated that in the chlorobenzenes the net charge at the carbon atom adjacent to chlorine is almost constant; equation (5) can therefore be written approximately as

$$q_z^{Cl} = [P_{xx}^{Cl} q_{xx}^{Cl} + P_{yy}^{Cl} q_{yy}^{Cl} + P_{zz}^{Cl} q_{zz}^{Cl}] + C \qquad (6)$$

where C is a constant. Our calculations further indicated that P_{xx}^{Cl} and P_{yy}^{Cl} are also almost constant $(=2)$, the z axis lying along the CCl bond; in that case the expression for the n.q.r. coupling constant of chlorine becomes:

$$e^2qQ = A P_{zz}^{Cl} + B \qquad (7)$$

where A and B are constants. In this derivation polarization of inner shell electrons (i.e. the Sternheimer[8] effect) has been neglected. If the range of field gradients is not large, as here, the effect should be to multiply the field gradient given by equation (1) by a constant factor; this will be absorbed into the empirical constants A and B in equation (7) which should consequently still hold.

Table 2 lists calculated values for P_{zz}^{Cl} and the observed ^{35}Cl n.q.r. coupling constants for the chlorobenzenes.

These were fitted to equation (7) by a least-squares procedure, leading to the relation:

$$e^2qQ = - 79·636\ P_{zz}^{Cl} + 184·102 \qquad (8)$$

The coupling constants calculated from equation (8) agree very well with experiment (correlation coefficient, 0·97; standard deviation, 0·048 MHz), considering that differential crystal-field effects can produce variations of as much as 0·5 MHz in ^{35}Cl coupling constants.

TABLE 2

Nuclear quadrupole coupling constants[a]

		e^2qQ (MHz)	
Compound	P_{zz}^{Cl}	Obs.	Calc.
Chlorobenzene	1·441701	69·24	69·29
p-Dichlorobenzene	1·432127	69·56	70·05
m-Dichlorobenzene	1·427307	69·80	70·44
1,2,4-Trichlorobenzene	1·414710	72·12	71·44
1,3,5-Trichlorobenzene	1·410457	71·70	71·78
o-Dichlorobenzene	1·408943	71·44	71·90
1,2,3,5-Tetrachlorobenzene	1·396673	73·92	72·88
1,2,3-Trichlorobenzene	1·395586	73·10	72·96
1,2,3,4-Tetrachlorobenzene	1·384360	74·68	73·86
1,2,4,5-Tetrachlorobenzene	1·381846	73·60	74·06
Pentachlorobenzene	1·366511	75·52	75·28
Hexachlorobenzene	1·337026	76·88	77·63

[a] Experimental coupling constants were obtained by doubling the resonance frequency. This data was taken from ref. 5, p. 185 and is for 77 K. If the line was a multiplet, the average was taken.

Equation (8) should refer to any chlorine atom in which $P_{xx}^{Cl} = P_{yy}^{Cl} = 2$; this should be the case for an isolated chlorine atom and for HCl. In the former, $P_{zz}^{Cl} = 1$; the corresponding coupling constant from equation (8) (104·5 MHz) agrees quite well with the accepted value (109·7 MHz[9]). In the case of HCl, a MINDO/2 calculation gave $P_{zz}^{Cl} = 1·623$; the corresponding value for the coupling constant (54·86 MHz) again agrees quite well with experiment (52·94 MHz[10]).

These results suggest that the MINDO/2 method may prove generally useful for the calculation of n.q.r. coupling constants, given that even a very simple approximation is so successful. In this preliminary form the method does not account well for asymmetry parameters; this, however, is not surprising since we have omitted all terms representing contributions by atoms other than that with the resonating nucleus. We are studying the inclusion of such terms, and the extension of the method to other nuclei; full details will be reported in due course.

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