

## THE $\alpha$ EFFECT IN CHLORINATED ORGANOMETALLIC COMPOUNDS

### I. $^{35}\text{Cl}$ NQR STUDIES OF PERCHLORINATED ORGANOMERCURIALS\*

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#### Summary

The  $^{35}\text{Cl}$  NQR spectra of mercurial- and organic-substituted pentachloro-cyclopentadienes are analyzed to give equations relating the frequencies of the allylic chlorines, Cl(5), and the two types of vinylic chlorine, Cl(1,4) and Cl(2,3), as functions of the Taft constant  $\sigma^*$  for R in  $\text{C}_5\text{Cl}_5\text{R}$ . Cl(5) in mercuri derivatives shows higher frequencies than Cl(5) in organic derivatives, but the magnitude of this frequency difference, a type of " $\alpha$  effect", decreases with increasing  $\sigma^*$ . This is best explained, not by previously-proposed theories of the  $\alpha$  effect, but by hyperconjugation of the Hg-C  $\sigma$  bond with diene  $\pi^*$  orbitals. The unusual NQR properties of trichloromethylmercurials, previously rationalized as due to an  $\alpha$  effect, are shown to be better explained by intermolecular coordination of Cl to Hg.

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#### Introduction

Organometallic compounds with heteroatom(s) and metal atom bonded to the same carbon atom ( $\alpha$ -hetero-organometallic compounds) [1] have unusual reactions such as (if the heteroatom is halogen [2])  $\alpha$ -elimination of metal halide to yield carbenes, and easy replacement of the halogen by nucleophiles [3]. Parallel to these reactions are unusual spectroscopic properties which have emerged from studies of  $\alpha$ -heteroorganometallics by  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{29}\text{Si}$  NMR [4-7], infrared spectra [8-10], UV spectra [11], dipole moments [5], mass spectra [12], boiling points [12], and NQR spectra [13-17]. Prominent among these properties have been reports of unusually high  $^{35}\text{Cl}$  NQR frequencies of (chloromethyl)silanes

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[13,14] and stannanes [15] and trichloromethylmercurials [16], and unusually low basicities of (alkoxymethyl)- [8] and (aminomethyl)-silanes [10]. These authors have termed these properties, which do not occur among  $\beta$ -,  $\gamma$ -, or other heteroorganometallics, the " $\alpha$  effect". Various chemical bonding rationalizations for the  $\alpha$  effect have been suggested.

Our interest in the NQR spectra of chlorinated organometallic compounds and our accumulation of NQR data on the pentachlorocyclopentadienylmercurials [18] (in which the allylic chlorine is located  $\alpha$  to mercury) has led us to examine that data for evidence of any unusual effects involving the allylic chlorines (in addition to organochlorine coordination) [6]. As NQR frequencies are influenced strongly by inductive effects, we began by studying the NQR frequencies of organic pentachlorocyclopentadienes,  $C_5Cl_5R$ , in order to determine the relationships between the frequencies for the various chlorines and the Taft polar substituent constant  $\sigma^*$  for R.

### Experimental procedure and assignment of spectra

The preparation and measurement of the 77 K NQR spectra of the pentachlorocyclopentadienylmercurials [18,19], organic pentachlorocyclopentadienes [18], and 1,2,3,4-tetrachlorocyclopentadiene [20] have previously been reported, and are collected in Table 1 of the preceding paper [18]. We prepared 5,5-dimethoxytetrachlorocyclopentadiene as described in the literature [21] and measured its NQR spectrum as previously described [18]. Values of  $\sigma^*$  were taken from the literature [22].

A complete analysis of these spectra requires the separation of the frequencies of the three chemically-distinct types of chlorine, Cl(1,4), Cl(2,3), and Cl(5) (see Fig. 1). This was done when possible, using the expectation that  $\nu(5)$ , the frequency of Cl(5), should be most sensitive to variations in  $\sigma^*$  of the organo group R.  $\nu(1,4)$  should be of intermediate sensitivity to  $\sigma^*(R)$ , while  $\nu(2,3)$  should be most nearly constant in value. But often we were only able to distinguish the allylic frequency  $\nu(5)$  from the other four vinylic frequencies.

The compounds  $C_5Cl_5H$  and  $C_5Cl_5(OCH_3)_2$  possess only vinylic chlorines, so that their frequencies (36.128 and 35.298 MHz for the former [20]; for the latter, 36.378, 36.976 (doubled intensity) and 37.055 MHz) establish the general range of vinylic frequencies. There is no apparent way to separate these spectra into  $\nu(1,4)$  and  $\nu(2,3)$ , so their averages have been calculated and listed in Table 1 as  $\bar{\nu}(\text{vinyl})$ , the average vinylic frequencies.

The spectra of the  $\alpha$  and  $\beta$  phases of  $C_5Cl_5$  have previously been reported [23]; the frequencies below 37.7 MHz were assigned [23] to vinylic chlorines

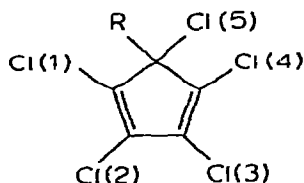


Fig. 1. Numbering system in pentachlorocyclopentadienes.

TABLE 1  
AVERAGES OF ASSIGNED NQR FREQUENCIES FOR  $\text{RC}_3\text{Cl}_5^a$

Compound	$\sigma^*(\text{R})$	$\bar{\nu}(\text{vinyl})$	$\bar{\nu}(2,3)$	$\bar{\nu}(1,4)$	$\bar{\nu}(5)$
$\text{C}_5\text{Cl}_4\text{H}_2^b$	-1.96 <sup>b</sup>	36.213			
$\text{C}_5\text{Cl}_5\text{HgCH}_2\text{C}_6\text{H}_5$		36.225 <sup>c</sup>	36.510	35.940	
$\text{C}_5\text{Cl}_5\text{HgC}_6\text{H}_5$		36.520 <sup>c</sup>	36.806	36.238	
$\text{C}_5\text{Cl}_5\text{C}(\text{CH}_3)_3$	-0.30				37.031
$\text{C}_5\text{Cl}_5\text{C}_2\text{H}_5$	-0.10	36.678	36.791	36.564	37.018
$\text{C}_5\text{Cl}_4(\text{OCH}_3)_2^b$	-0.04 <sup>b</sup>	38.846			
$\text{C}_5\text{Cl}_5\text{CH}_2\text{C}_6\text{H}_5$	0.215	36.763			37.709
$\text{C}_5\text{Cl}_5\text{H}$	0.49	36.964			38.019
$\text{C}_5\text{Cl}_5\text{CCl}_3$	2.65		37.085		39.430
$\text{C}_5\text{Cl}_5\text{Br}$	2.80	37.38	37.13	37.63	
$\text{C}_5\text{Cl}_6$	2.94	37.279			

<sup>a</sup> Frequencies in MHz, 77 K. Original data in ref. 18. All frequencies shifted by steric hindrance or effects of  $\alpha$ -substituent electron pairs are omitted.

<sup>b</sup> For  $\text{C}_5\text{Cl}_4\text{H}_2$  and  $\text{C}_5\text{Cl}_4(\text{CCH}_3)_2$ ,  $\sigma^*$  was calculated by deducting 2.94 for the missing Cl(5), then adding  $2 \times 0.49$  for the two allylic hydrogens, or  $2 \times 1.45$  for the two methoxy groups.

<sup>c</sup> From this data and eqn. 1  $\sigma^*$  is calculated as -2.33 for  $\text{R} = \text{HgCH}_2\text{C}_6\text{H}_5$  and -0.99 for  $\text{R} = \text{HgC}_6\text{H}_5$ .

and those above 38.8 MHz to Cl(5). Again a distinction between  $\nu(1,4)$  and  $\nu(2,3)$  cannot be made.  $\bar{\nu}(5)$  is not listed in Table 1, because it has been found that an  $\alpha$ -substituent with unshared electron pairs ( $\text{R} = \text{Cl}$  in this case) causes the NQR frequency of the geminal chlorine Cl(5) to be lowered in frequency from the value predicted from inductive effects alone [24]. Although most dramatic for fluorine, oxygen and nitrogen  $\alpha$ -substituents, the shift is still appreciable for chlorine and bromine [25].

The spectrum of  $\text{C}_5\text{Cl}_5\text{H}$  [18] is readily assigned on the basis of the spectrum of  $\text{C}_5\text{Cl}_5\text{D}$  [26], in which the 38.019 MHz line of Cl(5) is shifted to 38.004 MHz, whereas none of the four closely-spaced vinylic frequencies (36.887 to 37.090 MHz) are shifted by more than 1 kHz.  $\nu(1,4)$  and  $\nu(2,3)$  are indistinguishable.

From the intensity ratios (2/2/1) in  $\text{C}_5\text{Cl}_5\text{C}(\text{CH}_3)_3$  [18] we assign the highest frequency, 37.031 MHz, as  $\nu(5)$ . One or the other of the remaining lines belongs to a  $\nu(1,4)$  which is probably uncharacteristically high in frequency [20], as molecular models indicate steric strain between methyl groups and Cl(1,4). Hence we cannot use these vinylic frequencies in our computations.

Similarly,  $\text{C}_5\text{Cl}_5\text{CCl}_3$  is expected to show steric strain between one or two trichloromethyl chlorines and Cl(1,4). The spectrum [18] of  $\text{C}_5\text{Cl}_5\text{CCl}_3$  contains five lines with intensity ratios 2/2/1/1/2. By comparison with the spectra of  $\text{C}_5\text{Cl}_6$  and  $\text{CCl}_4$  [27] the two highest frequencies (39.756 and 40.762 MHz) can be assigned to the trichloromethyl group; the large splitting of these frequencies can be attributed to the steric strain affecting the two higher-frequency trichloromethyl chlorines [6]. The next frequency (intensity 1) must be  $\nu(5)$ . The second-lowest frequency, 37.907 MHz (intensity 2) is unusually high as compared to the other vinylic frequencies we have assigned, so it is attributed to the strained Cl(1,4) and discarded from calculations. Hence  $\nu(2,3)$  is found to be 37.085 MHz.

The compound  $\text{C}_5\text{Cl}_5\text{C}_2\text{H}_5$  crystallizes in two different solid phases [18]. The  $\alpha$  phase shows five lines with unusual intensity ratios: 36.275(S/N 44), 36.436(74), 36.734(44), 36.874(72), 37.174(23). But it is easily converted

[18] to the  $\beta$  phase with more nearly normal intensity ratios: 36.286(13), 36.754(17), 36.861(10), 36.961(13), 37.101(17). The other spectral properties of this sample are entirely consistent with the expected structure, so that we suggest that the unusual intensity ratios for the  $\alpha$  form may be due to wagging of the ethyl group, which would cause the closest chlorines to have the weakest, broadest signals. Using this hypothesis, we can assign the line of  $S/N$  23 to Cl(5); the two lines of  $S/N$  46 can be assigned to Cl(1,4), and the two strongest lines to the distant Cl(2,3). The same reasoning can be applied to the much less dramatic case of the  $\beta$  phase. By comparison with  $C_5Cl_5H$  and  $C_5Cl_5C_2H_5$  (of similar  $\sigma^*$  values) we assign the high-frequency 37.709 MHz line of  $C_5Cl_5CH_2C_6H_5$  [18] to Cl(5); the other four frequencies cannot be separated into  $\nu(2,3)$  and  $\nu(1,4)$ .

$C_5Cl_5Br$  gives broad and weak NQR signals, probably due to random orientation of Cl and Br in the crystal, or contamination by  $C_5Cl_6$ . The 39.26 MHz frequency is clearly  $\nu(5)$ , but it cannot be used in calculations due to the unshared electron pairs on Br. The four vinylic frequencies are separated by a large enough range to allow a tentative assignment of the 37.00 and 37.26 MHz frequencies to Cl(2,3), and the two higher frequencies to Cl(1,4). This is reasonable because most  $\nu(2,3)$  are quite close to 37.0 MHz\*.

The above assignments provide an ample number of  $\bar{\nu}(5)$  and  $\bar{\nu}(\text{vinyl})$  (Table 1), so that equations relating these to  $\sigma^*$  are derivable. More  $\bar{\nu}(1,4)$  and  $\bar{\nu}(2,3)$  are desirable, however. Examination of the spectra of the organomercurials [18] show two cases,  $C_5Cl_5HgCH_2C_6H_5$  and  $C_5Cl_5HgC_6H_5$ , in which the vinylic frequencies are split fairly clearly into two equal sets. The high set of vinylic frequencies of these compounds average 36.5 to 36.8 MHz, values likely for the relatively  $\sigma^*$ -insensitive  $\nu(2,3)$ , and are so assigned\*\*.

## Results

In the Experimental section we discuss the assignment of the 77 K NQR frequencies of the organic pentachlorocyclopentadienes to Cl(5), Cl(1,4), and Cl(2,3), or, when the latter two sets cannot be distinguished, to Cl(vinyl). The averaged assigned frequencies  $\bar{\nu}$  are presented in Table 1 along with  $\sigma^*$  values. Least-squares computations on these data produce the following correlations (with the correlation coefficients  $r$ ):

$$\bar{\nu}(\text{vinyl}) = (36.738 + 0.220 \sigma^* \pm 0.089) \text{ MHz}, r = 0.972 \quad (1)$$

$$\bar{\nu}(5) = (37.362 + 0.811 \sigma^* \pm 0.213) \text{ MHz}, r = 0.977 \quad (2)$$

$$\bar{\nu}(1,4) = (36.627 + 0.347 \sigma^* \pm 0.074) \text{ MHz}, r = 0.995 \quad (3)$$

$$\bar{\nu}(2,3) = (36.795 + 0.096 \sigma^* \pm 0.070) \text{ MHz}, r = 0.950 \quad (4)$$

\* The variable-temperature NQR for most of the above compounds was also examined [18]. For all compounds except the *gem*-dichloro compound  $C_5Cl_6$ , the frequency with the least dependence on temperature was the one which had been assigned to Cl(5). No difference in temperature-dependency could be ascertained between Cl(1,4) and Cl(2,3).

\*\* There appears to be little or no organochlorine coordination involving Cl(1,4): using data from Table 1 and other tentative but reasonable assignments of  $\nu(1,4)$ , a preliminary calculation of  $\bar{\nu}(1,4)$  as a function of  $\sigma^*$  was made. The  $\bar{\nu}(1,4)$  for  $R = HgCH_2C_6H_5$  and  $R = HgC_6H_5$  calculated with this preliminary equation agreed satisfactorily with the experimental frequencies, so the experimental frequencies were concluded to be shifted little or not at all by such coordination [18].

As mentioned in the Experimental section, there were difficulties in obtaining data points for eqns. 3 and 4, so that it is desirable to check their reasonableness. If we average them, we should, and do, obtain an equation which is very similar to the more firmly-grounded eqn. 1:

$$[\bar{\nu}(1,4) + \bar{\nu}(2,3)]/2 = (36.711 + 0.222 \sigma^* \pm 0.072) \text{ MHz} \cong \bar{\nu}(\text{vinyl}) \quad (5)$$

As a further check, we note that the coefficients of  $\sigma^*$ , which indicate the susceptibility to the inductive effect, decline in the order  $\bar{\nu}(5) > \bar{\nu}(1,4) > \bar{\nu}(2,3)$ , as they should. In aliphatic compounds, it has been suggested that the susceptibility to the effect drops off by a factor of 2.78 for each additional carbon atom separating the R group from the indicating group [22]. Applying this factor to the coefficient 0.811 for  $\bar{\nu}(5)$ , we predict coefficients of 0.292 for  $\bar{\nu}(1,4)$  and 0.105 for  $\bar{\nu}(2,3)$ , in satisfactory agreement with the experimental values.

As a final check, in Fig. 2 we plot all of the NQR frequencies, assigned or unassigned, for the organopentachlorocyclopentadienes as a function of  $\sigma^*$ . The frequencies should fall within  $\pm 1\%$  of the lines representing eqns. 2-4, as this is the limit of the scatter resulting from crystal-field effects in benzene-type compounds [28]. The only exception should be (a) sterically-hindered chlorines falling at higher frequencies [20], and (b) allylic chlorines with  $\alpha$ -halo neighbors falling below this range [25]. Compounds in which these exceptions are anticipated have been mentioned in the Experimental section, and are indicated in Fig. 2. It is seen that, with the expected exceptions, all frequencies do fall in the ranges predicted by eqns. 2-4.

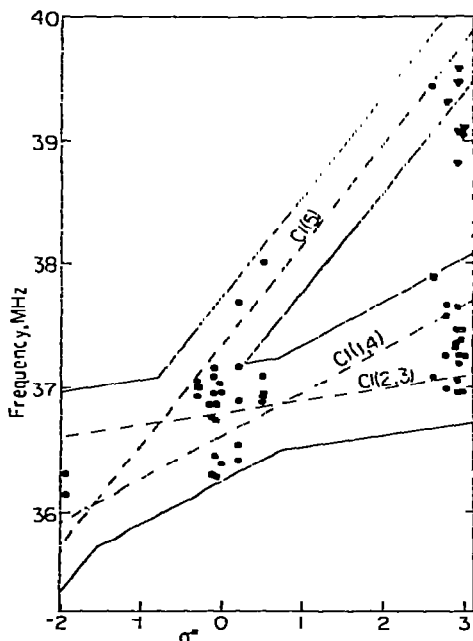


Fig. 2. NQR frequencies of organic pentachlorocyclopentadienes,  $C_5Cl_5R$ , as a function of  $\sigma^*(R)$ . Dots (●) represent normal frequencies; squares (■) represent frequencies expected to be high due to steric crowding; triangles (▲) represent frequencies expected to be low due to the effects of  $R = \text{halogen}$ . The dotted lines (---) represent eqns. 2, 3 and 4, which give average frequencies as a function of  $\sigma^*$ . The solid lines enclose a  $\pm 1\%$  scatter in eqns. 2-4 which is expected due to crystal lattice variations.

Equation 1 can now be solved for  $\sigma^*$ , giving eqn. 6 which can be used to obtain the  $\sigma^*$  values of mercuri groups from their  $\bar{\nu}(\text{vinyl})$ :

$$\sigma^* = 4.55 [\bar{\nu}(\text{vinyl}) - 36.738] \pm 0.4 \quad (6)$$

For many mercurials, however, we have found evidence that one-fourth of their vinylic chlorines have been shifted in frequency by intermolecular or intramolecular coordination [18]. In such a case a weighted average of eqns. 3 and 4 is more appropriate. If the coordinated chlorine is a Cl(1,4), eqn. 7 should be used; if it is a Cl(2,3), eqn. 8 is required. In either case  $\bar{\nu}(\text{vinyl})$  is calculated omitting the shifted frequencies.

$$\sigma^* = 5.42 [\bar{\nu}(\text{vinyl}) - 36.762] \pm 0.4 \quad (7)$$

$$\sigma^* = 3.84 [\bar{\nu}(\text{vinyl}) - 36.703] \pm 0.3 \quad (8)$$

In Table 2 we give the average  $\bar{\nu}(\text{vinyl})$  of the previously reported [18] frequencies of non-coordinating vinylic chlorines of the pentachlorocyclopentadienylmercurials. These averages are then substituted into eqn. 6, 7 or 8 to compute the  $\sigma^*$  values of the mercuri groups (Table 2). In the cases of coordination of vinylic chlorines, we do not know whether the coordinated chlorine is a Cl(1,4) or a Cl(2,3). Hence in such cases Table 2 contains  $\sigma^*$  values calculated both from eqn. 7 and eqn. 8. For this reason, we actually use values calculated

TABLE 2  
AVERAGE FREQUENCIES AND  $\sigma^*$  VALUES FOR  $C_5Cl_5HgX$

(1) Mercuri group	(2) $\bar{\nu}(\text{vinyl})$ (MHz) <sup>a</sup>	(3-6) $\sigma^*$ calc. using eqn.				(7) $\bar{\nu}(5)$ Calc. <sup>d</sup>	(8) $\bar{\nu}(5)$ Obs <sup>a</sup>
		6 <sup>b</sup>	7	8	6 <sup>c</sup>		
HgCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	36.225	-2.3				35.47	e
HgC <sub>5</sub> Cl <sub>5</sub> · 5/3glyme	36.514	-1.0				36.54	38.555
HgC <sub>6</sub> H <sub>5</sub>	36.520	-1.0				36.56	e
HgBr · diglyme	36.542	-0.9				36.64	38.406
HgCl · diglyme	36.580	-0.7				36.78	38.364
HgC <sub>5</sub> Cl <sub>5</sub> · 2THF	36.595	-0.6				36.84	e
HgBr · triglyme	36.596	-0.6				36.84	38.687
HgCl · triglyme	36.600	-0.6				36.85	38.742
HgBr · glyme	36.671	-0.3	-0.5	-0.1	-0.7	37.12	38.654
HgCl · glyme	36.679	-0.3	-0.4	-0.1	-0.8	37.14	38.696
HgC <sub>5</sub> Cl <sub>5</sub> -β	36.74 <sup>f</sup>	0.0	-0.1	0.1	-0.2	37.35	e
HgC <sub>5</sub> Cl <sub>5</sub> -α	36.844	0.5	0.4	0.5	-0.1	37.75	38.960
HgC <sub>5</sub> Cl <sub>5</sub> -γ	36.882	0.7	0.6	0.7	0.2	37.90	e
HgCl · 1/2THF	36.970	1.1				38.22	39.394
HgCl-α	37.09 <sup>f</sup>	1.6	1.8	1.5	0.7	38.66	39.25 <sup>f</sup>
HgBr	37.104	1.7	1.9	1.5	0.3	38.72	e
HgCl-γ	37.117	1.7	1.9	1.6	0.2	38.73	e
HgCl-β	37.144	1.8				38.86	39.387
HgBr · HgBr <sub>2</sub>	37.264	2.4	2.7	2.2	1.3	39.30	e
HgCl · HgCl <sub>2</sub>	37.281	2.5	2.8	2.2	1.3	39.36	e

<sup>a</sup> Calculated from data in ref. 18, omitting frequencies assigned to coordinating chlorines. <sup>b</sup> Using data from column 2, this table. <sup>c</sup> Using data calculated from ref. 18, including frequencies assigned to coordinating chlorines. <sup>d</sup> Using data from column 3 (before rounding off) and eqn. 2. <sup>e</sup> All chlorines are coordinating, hence omitted. <sup>f</sup> Extrapolated from room temperature NQR spectra.

form eqn. 6, which gives results approximately midway between those obtained from eqns. 7 and 8, with an additional uncertainty up to  $\pm 0.3^*$ .

The resulting  $\sigma^*$  values, although mathematically not critical to the examination of the  $\alpha$  effect, [an equation for  $\bar{\nu}(5)$  could be derived in terms of  $\bar{\nu}(\text{vinyl})$  only by eliminating  $\sigma^*$  between eqns. 2 and 6] are quite satisfying on two counts\*\*. First, they show a chemically-reasonable order of increasing electron-withdrawing power:  $\text{HgCH}_2\text{C}_6\text{H}_5 < \text{HgC}_6\text{H}_5 < \text{HgC}_5\text{Cl}_5 < \text{HgBr} < \text{HgCl}$  and  $\text{HgX} \cdot \text{Lewis base (base = ether)} < \text{HgX} < \text{HgX} \cdot \text{Lewis acid (acid = HgX}_2)$ . Secondly, for different phases of the same compound, we have (within experimental error) the same inductive constant for the same HgX group: the three  $\text{HgC}_5\text{Cl}_5$  phases all give  $\sigma^*$  values of 0.0 to 0.7 (the 0.0 value being based on extrapolated data); the four HgX phases all give  $\sigma^*$  values of 1.6 to 1.8\*\*\*.

We can now substitute the  $\sigma^*$  values of mercuri groups (column 3) into eqn. 2 to obtain the  $\bar{\nu}(5)$  that we would expect in the mercurials on the basis of the inductive effect alone; these are listed in column 7 of Table 2. Column 8 lists the averages of the observed frequencies, omitting those believed to be shifted by inter- or intra-molecular coordination [18]. It may be seen that the actual frequencies are not at all close to the calculated ones: there is an  $\alpha$  effect in the pentachlorocyclopentadienylmercurials.

The observed  $\bar{\nu}(5)$  are found to be a function of  $\sigma^*$ , and fit the correlation 9 rather than 2. The magnitude of the  $\alpha$  effect, i.e., the amount of deviation of  $\bar{\nu}(5, \text{Hg})$  from the inductively-caused frequency, can be obtained by subtracting eqn. 2 from eqn. 9:

$$\bar{\nu}(5, \text{Hg}) = [38.811 + 0.338 \sigma^* \pm 0.125] \text{MHz}, r = 0.941 \quad (9)$$

$$\alpha \text{ effect} = \bar{\nu}(5, \text{Hg}) - \bar{\nu}(5) = (1.449 - 0.473 \sigma^*) \text{MHz} \quad (10)$$

Alternatively it can be obtained by subtracting column 7 of Table 2 from column 8.

Hence we come to two very interesting results: (a) there is an  $\alpha$  effect in this series of compounds, which results, as in previous studies [13-17], in unexpectedly high NQR frequencies; (b) the magnitude of this  $\alpha$  effect decreases with increasing electron-withdrawing ability of the mercuri group.

\* The use of eqn. 6 also has the effect of removing dependency of the  $\sigma^*$  values on the less-reliable eqns. 3 and 4, as it is not derived from them.

\*\* The agreement between these  $\sigma^*$  values and those obtained by the more usual method of  $^{19}\text{F}$  NMR of *m*- and *p*- $\text{FC}_6\text{H}_4\text{HgX}$  in solution (values calculated from data in ref. 30) ranges from fairly good for electron-withdrawing substituents to quite poor for electron-donating groups. However, the hybridization used by mercury is thought to depend on the nature of the groups attached to it [31]. In the case of the substituent Hg-aryl, say, it would then be invalid to compare the results of  $^{19}\text{F}$  NMR of *m,p*- $(\text{FC}_6\text{H}_4)_2\text{Hg}$ , which contains only relatively electron-donating groups attached to mercury, to the results of NQR of  $\text{C}_6\text{H}_5\text{HgC}_5\text{Cl}_5$ , which also contains an electron-withdrawing group.

\*\*\* If we totally ignore the possibility of coordination of vinylic chlorines in these mercurials, we can calculate the average frequency of all vinylic chlorines, coordinated or not, and use eqn. 6 to obtain the values of  $\sigma^*$  obtained in column 6 of Table 2. For the four HgX phases we then obtain  $\sigma^* = 0.7, 0.2, 0.3, 1.8$ , an inconsistent result which shows the importance of taking into account organochlorine coordination in chlorinated organomercurials [18].

Theories of the  $\alpha$  effect

The observed low basicity of (alkoxymethyl)- [8] and (aminomethyl)- [10] silanes and the high NQR frequencies of  $\alpha$ -chloroalkylmetal systems have been explained by hypotheses based on ground-state electron withdrawal from the heteroatom O, N or Cl. Three sources of these electrons have been suggested: (a) the unshared electron pair(s) [5] on the chlorine atom or other heteroatom, which we shall symbolize  $n(\text{Cl})$ ; (b) the carbon—chlorine sigma-bonding electron pair [13],  $\sigma(\text{C—Cl})$ ; or (c) in compounds of the type  $\text{XCH}_2\text{MR}_n$ , the carbon—hydrogen sigma-bonding electrons [32]. Only the first two sources could apply to the perchloro compounds discussed in this paper. Two types of orbitals have been suggested as the electron acceptors: (a) the empty  $d$  orbitals on silicon [5, 9,12-14] or  $p$  orbitals on mercury [16,17] which we shall abbreviate  $p(\text{Hg})$ ; (b) the carbon—metal antibonding orbitals [32],  $\sigma^{-1}(\text{C—Hg—R})$ . Hence we have four possible combinations of donor—acceptor interactions: (I)  $n(\text{Cl}) \rightarrow p(\text{Hg})$ , (II)  $n(\text{Cl}) \rightarrow \sigma^{-1}(\text{C—Hg—R})$ , (III)  $\sigma(\text{C—Cl}) \rightarrow p(\text{Hg})$ , and (IV)  $\sigma(\text{C—Cl}) \rightarrow \sigma^{-1}(\text{C—Hg—R})$ . These interactions are drawn schematically in Fig. 3. One other type of interaction has recently been suggested, a three-center bond involving the  $\sigma$ -bonding orbital of chlorine, the carbon  $\sigma$ -bonding orbital which is directed at chlorine, and a silicon  $d$  orbital [14]. This slight variation on interaction (III) we shall call (IIIa).

In the cyclopentadienylmercurials we have other vacant orbitals which are potentially acceptors, the antibonding  $\pi$  orbitals of the diene ring,  $\pi^{-1}(\text{C}_5\text{Cl}_5)$ . Hence we can add more hypothetical interactions: (V)  $n(\text{Cl}) \rightarrow \pi^{-1}(\text{C}_5\text{Cl}_5)$ , and (VI)  $\sigma(\text{C—Cl}) \rightarrow \pi^{-1}(\text{C}_5\text{Cl}_5)$ . Finally, there is evidence [19] for a hyperconjugative interaction between the ring—mercury  $\sigma$  bond and the antibonding  $\pi^{-1}$  orbital, which we can label (VII)  $\sigma(\text{C}_5\text{Cl}_5\text{—Hg}) \rightarrow \pi^{-1}(\text{C}_5\text{Cl}_5)$ .

According to the Townes—Dailey approximation [24b] the NQR frequency

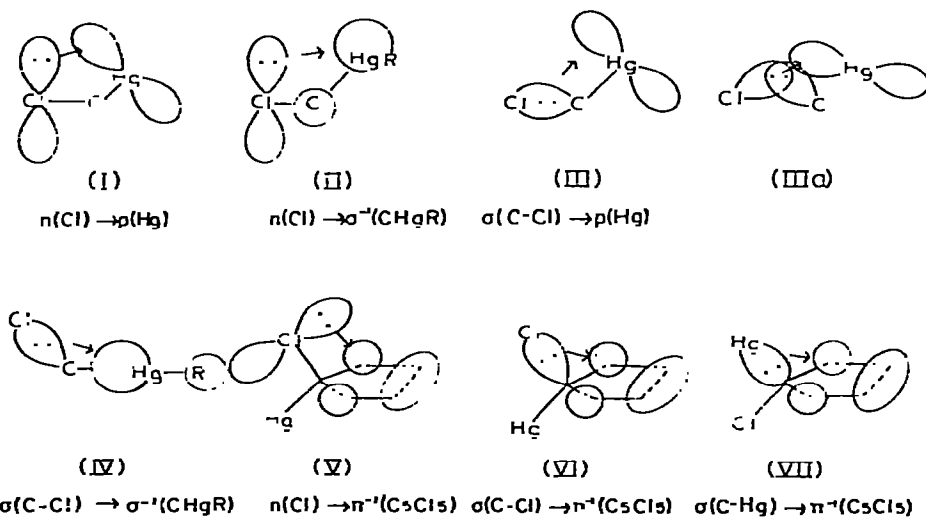


Fig. 3. Schematic drawings of the interactions proposed to account for the  $\alpha$  effect. For explanation see text.



of a covalently bonded chlorine atom is given by eqn. 11, where  $N_x$  and  $N_y$  are

$$\nu = \frac{109.746}{2} \left( \frac{N_x + N_y}{2} - N_z \right) \quad (11)$$

the populations of the chlorine's lone-pair orbitals  $p_x$  and  $p_y$ , and  $N_z$  is the  $p_z$  population;  $p_z$  being the main component of the chlorine  $\sigma$ -bonding orbital. Removing electrons from the  $p_x$  and  $p_y$  lone pairs would lower the NQR frequency, contrary to all observations [13-17]. Hence we can eliminate the hypotheses of interactions (I), (II), and (V), or at least state that if they occur, they are totally masked by some other, larger interaction.

Interactions (III), (IIIa), (IV), and (VI) are compatible with eqn. 11 and the observed high frequencies. Interaction (VII) is also compatible, for two reasons: electron-transfer from the carbon-5—mercury bond to the  $\pi^{-1}$  orbital, located principally on carbon atoms 1,2,3 and 4, will cause an indirect inductive withdrawal of electrons from Cl(5). Probably of greater importance, interaction (VII) will be increased if the mercury— $C_5Cl_5$   $\sigma$  bond utilizes a great deal of carbon  $2p$  character, as this will facilitate overlap with the  $\pi^{-1}$  orbital [34]. This causes the carbon-5—chlorine-5 orbital to make greater use of the more electro-negative carbon  $2s$  orbital, which removes electrons from chlorine. A somewhat analogous phenomenon is known to happen in the NQR of cyclopropyl chlorides, in which the orbital electronegativity of the carbon orbitals directed at chlorine are particularly high, giving rise to NQR frequencies which are about 2 MHz higher than in analogous isopropyl chlorides [35].

Next we consider, in a system Cl—C—Hg—R, the effect of increasing the inductive electron-withdrawing power ( $\sigma^*$  value) of the group R attached to mercury. As  $\sigma^*(R)$  increases, the  $p$  orbitals of mercury should be lowered in energy and/or contracted in size so that they are better able to interact with other orbitals; this is seen, for example, in the ability of  $HgCl_2$  but inability of  $Hg(CH_3)_2$  to form complexes by adding additional ligands. Hence interaction (III) or (IIIa) should lead to an increasing  $\alpha$  effect with increasing  $\sigma^*(R)$ ; the opposite is observed\*.

The hypothesis of interaction (IV) also fails: as the energy of the  $\sigma$ -bonding orbital of the substituent R drops further below that of mercury, the energy of the Hg—R antibonding orbital should drop [33] (since the overlap integral, which raises the antibonding orbital above the original mercury orbital in energy, becomes smaller). This lower-energy  $\sigma^{-1}(C-Hg-R)$  should be more electronegative and overlap the  $\sigma(CCl)$  better, giving an increasing  $\alpha$  effect — which is not observed.

With interaction (VI), an electron-withdrawing R group should inductively lower in energy both the  $\sigma(C-Cl)$  and  $\pi^{-1}(C_5Cl_5)$  orbitals, hence perhaps affecting their overlap little. There would also be a greater probability of finding the C—Cl  $\sigma$ -bond electrons on carbon, a situation which should favor hyperconjugation.

\* If interaction (III) were a valid hypothesis, we might expect that the  $\alpha$  effect would be diminished in the adducts of the polyethers glyme, diglyme, and triglyme, since these ethers would compete with (III) by coordinating to mercury via its  $p(Hg)$  orbitals. The adducts, however, show no reduction in  $\alpha$  effect.

tion of this bond with  $\pi^{-1}$  [34]. Hence the effect of increasing  $\sigma^*(R)$  on an  $\alpha$  effect resulting from interaction (VI) is uncertain.

Interaction (VII) should be reduced by a more electron-withdrawing substituent R: this lowers the energy of the  $C_5Cl_5-Hg$   $\sigma$  bond, which increases its mismatch with the higher-energy  $\pi^{-1}(C_5Cl_5)$  orbital. We have previously shown [19] by UV spectroscopy that interaction (VII) decreases with increasing electron-withdrawing power of R. Hence only (VII) clearly produces the correct prediction, a decreasing  $\alpha$  effect with increasing  $\sigma^*(R)$ .

To check this conclusion, we correlated the magnitude of the  $\alpha$  effect, obtained as the difference of columns 7 and 8 of Table 2 when possible, or from eqn. 10 when necessary, with the separation of the  $\pi_1$  and  $\pi_2$  orbitals of the ring system, (an inverse measure of interaction VII) [19]. There is an inverse correlation,  $r = -0.910$ .

Hence we conclude that the hypotheses of interaction (VII) is the best single explanation of the  $\alpha$  effect in the pentachlorocyclopentadienylmercurials, with interaction (VI) being an outside possibility. Beyond these it is possible that some combination of two or more interactions could also explain this data, particularly if the second interaction were some sort of back-donation to chlorine. However, Occam's Razor leads us to prefer the single hypothesis, particularly as it is not a novel one, but is established [19,34].

### The $\alpha$ effect in trichloromethylmercurials

The  $\alpha$  effect in organomercurials was originally suggested on the basis of the NQR spectra of the trichloromethylmercurials [16,17]. As our explanation (hypothesis VII) cannot apply to these compounds, we have had to find an alternative hypothesis to explain these NQR spectra. Principally because of unusually large splittings of the NQR frequencies of  $CCl_3HgBr$ ,  $CCl_3HgCl$  and  $(CCl_3)_2Hg$ , the absence of these splittings in the glyme adducts of these molecules [17], and an X-ray structure of  $CCl_3HgBr$  [16], Semin proposed that the higher frequencies of the unusually-split NQR spectra were caused by an  $\alpha$  effect. Presumably, then, the lower frequencies in these spectra are "normal". However, we were also able to account for these features by postulating that intermolecular coordination is responsible for the lower frequencies of the unusually-split NQR spectra [18]. Our hypothesis implied that the higher frequencies were "normal", i.e., produced by inductive effect alone.

The  $\sigma^*$  values of mercuri substituents in  $CCl_3HgX$  cannot be determined, then, from the NQR spectra of these compounds alone, due to the ambiguity as to which frequencies are normal. However, we feel that these  $\sigma^*$  values should be rather similar to those just determined for the  $C_5Cl_5HgX$  series. Except for the presence of the hyperconjugative interaction VII in the  $C_5Cl_5HgX$  series, the two chlorocarbon groups should be rather similar in their interactions with mercurial substituents\*. (The hyperconjugation may result in a hybridization other than pure  $sp^3$  for carbon-5, but there is no evidence to lead one to expect

\* From various NQR data, we have estimated  $\sigma^*(C_5Cl_5) = 2.4 \pm 0.4$ , which compares in magnitude with  $\sigma^*(CCl_3) = 2.65$  [22].

any change in the hybridization or other electronic properties of the mercury atom or its substituent.) Hence we should be able to find a good correlation of the  $\sigma^*$  values from the  $C_5Cl_5HgX$  series and the values derived from the truly "normal" frequencies of the trichloromethylmercurials; furthermore, the two sets of  $\sigma^*$  values should agree well in magnitude.

If the abnormal frequencies are abnormal due to an  $\alpha$  effect, we should find that  $\sigma^*$  values calculated from them show poor agreement with the values obtained from  $C_5Cl_5HgX$ . But the two sets of values probably should correlate well, as the  $\alpha$  effect is likely a function of  $\sigma^*$ . On the other hand, if the abnormal frequencies are caused by intermolecular coordination, they should give neither a good agreement of  $\sigma^*$  values, nor a good correlation, since intermolecular coordination is quite dependent on steric factors.

Voronkov [29] has derived eqn. 12 by which we can obtain  $\sigma^*(X)$  from the (normal) NQR frequency of  $CCl_3HgX$ :

$$\sigma^*(X) = 0.9987\{\bar{\nu}(CCl_3) - 37.87\} \pm 0.10, r = 0.927 \quad (12)$$

We have divided the abnormally-split NQR frequencies reported in the literature [17] for  $CCl_3HgX$  into sets of high and low frequencies; the average frequencies of these sets are listed in Table 3, columns 3 and 5. From these average frequencies and eqn. 12 values have been computed (columns 4 and 6). The  $\sigma^*$  values computed from the high frequencies show a good correlation with those computed for  $C_5Cl_5HgX$ ,  $r = 0.967$ ; the two sets also agree in magnitude. The values of column 4 also make good chemical sense, i.e.,  $\sigma^*(HgC_6H_5) < \sigma^*(HgCCl_3) < \sigma^*(HgBr) < \sigma^*(HgCl)$  and  $\sigma^*(HgX \cdot \text{ether}) < \sigma^*(HgX)$ . Hence the high frequencies appear to be the "normal" ones.

The  $\sigma^*$  values computed from the low frequencies (column 6), on the other hand, correlate poorly with those based on  $C_5Cl_5HgX$ ,  $r = 0.267$ . There is little chemical sense in these values in that  $\sigma^*(HgX \cdot \text{ether})$  may be less than or greater than  $\sigma^*(HgX)$ . We conclude that the low frequencies show the irregularities expected to result from intermolecular coordination and that the overall

TABLE 3

$\sigma^*$  VALUES FOR MERCURI GROUPS DERIVED FROM NQR DATA ON  $C_5Cl_5HgX$  AND  $CCl_3HgX$

(1) Substituent type HgX	(2) $C_5Cl_5HgX$ $\sigma^*$	$CCl_3HgX$ high frequencies		$CCl_3HgX$ low frequencies	
		(3) $\bar{\nu}$	(4) $\sigma^*$	(5) $\bar{\nu}$	(6) $\sigma^*$
$HgC_6H_5$	-1.0	37.125 <sup>a</sup>	-0.7	36.424 <sup>a</sup>	-1.4
$HgC_nCl_m \cdot \text{glyme}$	-1.0	37.348	-0.6	37.348	-0.6
$HgC_nCl_m \cdot THF$	-0.6	37.482	-0.4	37.482	-0.4
$HgCl \cdot \text{diglyme}$	-0.7	37.490 <sup>b</sup>	-0.4	37.490 <sup>b</sup>	-0.4
$HgBr \cdot \text{glyme}$	-0.3	37.710	-0.2	37.710	-0.2
$HgCl \cdot \text{glyme}$	-0.3	38.11	0.2	38.11	0.2
$HgBr \cdot \text{dioxane}$	-	38.054	0.1	36.818	-1.1
$HgC_nCl_m$	0.6	38.675	0.8	37.358	-0.6
$HgBr$	1.7	38.913	1.0	37.744	-0.2
$HgCl$	1.7	39.102	1.2	37.786	-0.1

<sup>a</sup> All data not footnoted are computed from spectra given in ref. 16. <sup>b</sup> Prepared by us (stoichiometry of diglyme/ $CCl_3HgCl$  not measured), and observed to give the following spectrum: 37.295 MHz (S/N 18), 37.532 MHz (18), 37.643 MHz (18), temperature 77 K.

pattern of frequencies and  $\sigma^*$  values is more consistent with the hypothesis of the presence of intermolecular coordination in the trichloromethylmercurials than with the presence of an  $\alpha$  effect\*.

Hence we conclude that, for the trichloromethylmercurials, the NQR spectra and other features can be explained entirely without recourse to any  $\alpha$  effect. We have not disproved its existence in these compounds — it certainly could be hidden beneath the larger effects of organochlorine coordination. But there is no evidence which uniquely favors an  $\alpha$  effect in the ground state of trichloromethylmercurials; and the type of " $\alpha$  effect" found for pentachloro-cyclopentadienylmercurials (interaction VII) is not at all what one usually means by this term. Hence, at least in perchlorinated organomercurials, one must doubt the necessity of theories of an  $\alpha$  effect.

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\* There is one other objectionable feature to Semin's hypothesis: the NQR spectrum of  $(CCl_3)_2Hg$  shows three lines, at 37.037, 37.680 and 38.675 MHz (all of equal intensity) [16]. In the absence of intermolecular effects this molecule should have a threefold symmetry axis, in which case the  $p_x(Hg)$  and  $p_y(Hg)$  orbitals are degenerate and should interact equally with all  $\alpha$  chlorines, producing no large splitting. The observed large splitting must then be due primarily to solid-state intermolecular organochlorine coordination.

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