CHLORINE NQR SPECTRA OF SOME BENZYL CHLORIDES, ALLYL CHLORIDES, AND CHLOROPHOSPHINES

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Abstract—Cl^{35} nuclear quadrupole resonance (NQR) spectra are reported for a number of substituted benzyl chlorides and allyl chlorides, for *o, m,* and *p*-chloroacetophenone, and for phenyldichlorophosphine and its *p*-chloro derivative. The results for the benzyl chlorides imply a large hyperconjugative interaction between the ring and the CCl bond.

INTRODUCTION

SINCE phenyl is electron withdrawing relative to hydrogen,[1] one would expect the Cl^{35} NQR signal from benzyl chloride to appear at a higher frequency than that (34·023 MHz[2]) from MeCl; in fact it is less (33·627 MHz[3]). This discrepancy is undoubtedly due to a hyperconjugative interaction between phenyl and the CCl bond that could be symbolized in resonance terminology by a contribution by the ionic resonance structure $(PhCH_2{}^+ Cl^-)$. Similar lowering of the Cl^{35} NQR frequency might be anticipated in other compounds RCl where R^+ is stabilized by any kind of mesomeric interaction; a recent paper[4] described studies of a number of chloronorbornanes and chloronorbornenes in the hope of observing such an effect. Here we report measurements of Cl^{35} NQR spectra of various organic chlorides where conjugative effects might be important.

The first series of compounds were substituted benzyl chlorides. If the Cl^{35} frequency of $PhCH_2Cl$ is in fact reduced by incipient ionization, the effect should be augmented by $-E$ or $-I$ substituents in the phenyl group. Since the NQR frequencies of substituted chlorobenzenes follow the Hammett relation,[5] one might expect the same to be true of substituted benzyl chlorides if resonance interactions between the substituent and the chloromethyl group are unimportant. If therefore participation by the ionic structure $(PhCH_2{}^+ Cl^-)$ is important, or potentially important, one might expect substituted benzyl chlorides to obey the Hammett relation for substituents of $+E$ or $+I$ type, but to show increasing deviations with increasingly $-E$ or $-I$ substituents. In connection with this work, the NQR spectra of several allyl chloride derivatives, and of 9-chlorofluorene, were also measured.

A second study was concerned with the effect of *p*-acyl substituents on the Cl^{35} frequency of chlorobenzene. Bray and Barnes[5] had reported values for *p*-chloroacetophenone and *p*-chloropropionophenone which seemed unreasonable, implying that the acyl behaves as an electron-releasing group.

A third project was concerned with the possible transmission of substituent effects through phosphorus by $p\pi:d\pi$ bonding; a number of substituted phenyldichlorophosphines were studied but unfortunately only the parent compound, and its *p*-chloro derivative, gave detectable signals.

Measurements are also reported for several other compounds where we believe the values reported in the literature to be in error.

RESULTS

The measurements were made at 77°K, using a modified super-regenerative spectrometer of the type described by Peterson and Bridenbaugh.[6] The resonant frequencies

TABLE I. Cl^{33} NQR FREQUENCIES AT 77°K FOR VARIOUS CHLORIDES

Compound	Cl^{35} NQR frequency (MHz)[a]	Signal/noise	Literature Values (MHz)
Benzyl chloride (1)	33·630	35	33·627[b]
2-Methylbenzyl chloride (2)	33·605	46	—
2,5-Dimethylbenzyl chloride (3)	34·046	13	—
2,4,6-Trimethylbenzyl chloride (4)	33·149[c]	5	—
2-Nitrobenzyl chloride (5)	34·593	17	—
3-Nitrobenzyl chloride (6)	34·215	10	34·216[d]
4-Nitrobenzyl chloride (7)	34·284[c]	36	34·311[e]
4-Fluorobenzyl chloride (8)	33·511[f]	7	—
o-Xylylene dichloride (9)	34·378[c]	3	...
p-Xylylene dichloride (10)	33·874[c]	25	33·863[e]
2-Chlorobenzyl chloride (11)	34·350	6	34·560, 34·795,
	34·848	15	35·225[e]
3-Chlorobenzyl chloride (12)	33·891[c]	3	see
	34·431	5	text
4-Chlorobenzyl chloride (13)	33·754	16	33·754[g]
	34·564	16	34·567[g]
2,3-Dichloropropene (14)	34·266	28	—
	35·100[g]	30	—
3-Chloro-2-chloromethylpropene (15)	33·700	23	—
Cis-3,4-dichlorocyclobutene (16)	33·838	40	—
	34·165	38	—
2-Chloroacetophenone (17)	35·788	9	35·760[i]
3-Chloroacetophenone (18)	35·181	3	—
4-Chloroacetophenone (19)	35·111[c]	4	34·618[j]
Chlorokojic acid (20)	35·830[c]	4	—
9-Chlorofluorene (21)	34·480	4	
Phenyldichlorophosphine (22)	26·244[h]	16	—
	26·539[c]	22	—
4-Chlorophenyldichlorophosphine (23)	26·357	3	...
	26.576	5	—
	34·933[c]	4	—
	35·102	3	...

[a] Estimated error ±0·001 MHz except where otherwise noted.

[b] R. Livingstone. *J. Phys. Chem.* **57**, 496 (1953)

[c] Estimated error, ±0·002 MHz.

[d] H. O. Hooper and P. J. Bray, *J. Chem. Phys.* **33**, 334 (1960)

[e] P. J. Bray and J. Ring, *J. Chem. Phys.* **21**, 2226 (1953)

[f] Estimated error, ±0·011 MHz.

[g] H. C. Meal, *J. Amer. Chem. Soc.* **74**, 6121 (1952)

[h] Estimated error, ±0·003 MHz.

[i] I. P. Birukov, M. G. Voronkov and I. A. Safin, *Tabitsy Chastot Iadernogo Kuadrupalnogo Resonanza*, Izdatelystvoe "Khimiya" *Leningradskoe Oldelenie* (1968)

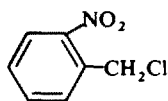[j] P. J. Bray and R. G. Barnes, *J. Chem. Phys.* **27**, 551 (1957)

were determined with a spectrum analyser and frequency counter. Most of the compounds were commercial samples, used without further purification. The dichlorocyclobutene (**16**) was supplied by Professor R. Pettit and the two phenyldichlorophosphines (**22** and **23**) by Professor A. Cowley.
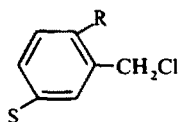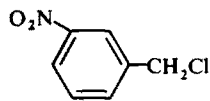

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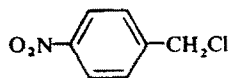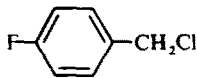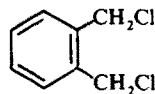2 R = CH$_3$, S = H
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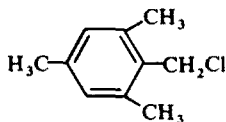
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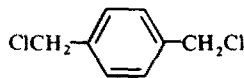
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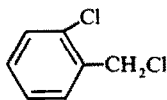
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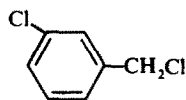
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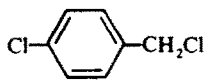
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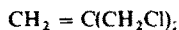
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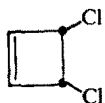
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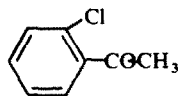
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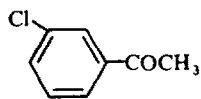
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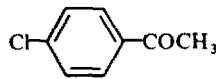
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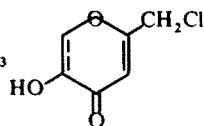
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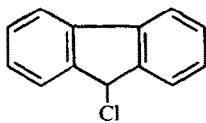
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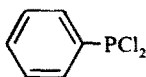
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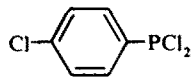
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Our values for **1, 6,** and **13** agree closely with those previously reported. In the case of **7, 10** and **17** there are significant discrepancies; these are probably due to incorrect identification of the parent signal among the collection of sidebands separated from it by the quench frequency. Since the technique of Peterson and Bridenbaugh,[6] which we used, is superior in this connection to those available previously, we believe our values to be the more reliable.

Our spectrum of **12** consisted of two areas of resonance the second of which, at *ca.* 34·4 MHz, seemed to contain two unresolved peaks. Saito found no signal for this compound at 33·9 MHz, but observed several at higher frequencies which came and went with changing experimental conditions.[7] Using material crystallized slowly at 5°C, he observed two lines at 34·426 and 34·622 MHz. When the sample was held for

some time at liquid N_2 temperature, i.e. conditions similar to those used by us, he claimed that additional signals appeared at 34·683, 34·875, and 35·050 MHz. Although our spectrum was not ideal, it was fully reproducible and, as will be seen presently, our observed frequencies are close to those expected from analogy with the other compounds studied. We cannot account for the discrepancy with Saito's work.

Similar remarks apply to **19** where our observed frequency (35·111 MHz) differs from that (34·618 MHz) of Bray and Barnes[5] by 0·5 MHz. The situation is further complicated by the close agreement between the frequencies found by Bray and Barnes[5] for **19** and for the corresponding propionyl derivative (34·702 MHz). As pointed out in the introduction, these values would imply that p-acetyl and p-propionyl are electron releasing groups, the corresponding σ constants, using the Bray–Barnes relation,[5] being −0·20 and −0·12 respectively. Our values for the NQR resonances of **18** and **19** lead to σ constants for m- and p-acetyl of +0·35 and +0·28 respectively, in reasonable agreement with the literature values (+0·31 and +0·52).[8]

The final discrepancy concerns **11**. Here our values were so different from those reported in the literature[9] that we suspected the identity of our sample. This, however, was confirmed by elemental analysis and by its NMR and IR spectra. The NQR spectrum was very clean, consisting of two clear and easily measured peaks. Saito[7] has suggested that the reported[9] value of 35·225 MHz may be a typographical error for 34·225; in that case the remaining discrepancies could perhaps be due to incorrect identifications of sidebands. Here we have no doubt that our values are correct.

DISCUSSION

In the case of the chlorobenzyl chlorides **11–13**, it is necessary to identify the two chlorine signals.

Beidenknapp and Weiss[10] have extended the work of Bray and Barnes[5] on substituent effects by introducing a new set of substituent constants (κ) specifically intended to account for NQR chemical shifts. In terms of these, the Cl^{35} NQR frequency (ν) of a substituted chlorobenzene is given by

$$\nu = 34·695 + \sum_i \kappa_i \tag{1}$$

The data in Table I for substituted benzyl chlorides other than **11–13** follow a similar relation, with the final sum multiplied by a factor of ca. 0·4. Using the κ values[10] for o-, m-, and p-chloro, we arrive at estimates of 34·11, 33·80, and 33·84 MHz for the sidechain chlorines in **10, 11** and **12** respectively. The close agreement between these values and the lower of the two observed resonances in each case (34·35, 33·89, and 33·75 MHz) makes it very likely that this identification is correct. In each case the discrepancy between the calculated value and the higher frequency is too large to be easily attributed to crystal field effects. With this identification, we can then use the higher observed frequencies to arrive at estimates of the κ constants for o-, m-, and p-CH_2Cl; viz.

$$o\text{-}CH_2Cl, \ +0·153; \quad m\text{-}CH_2Cl, \ -0·264; \quad p\text{-}CH_2Cl, \ -0·131 \tag{2}$$

Including the values for **10, 11,** and **12**, a least squares fit led to the following

relation between the Cl^{35} NQR frequency of the sidechain chlorine and κ;

$$\nu(CH_2Cl; MHz) = 33.767 + 0.393 \sum_i \kappa_i \qquad (3)$$

Table II compares the observed values of ν with those calculated from equation (3).

TABLE II. COMPARISON OF CALCULATED AND OBSERVED Cl^{35} FREQUENCIES FOR SUBSTITUTED BENZYL CHLORIDES

Compound	$\sum_i \kappa_i{}^a$	NQR frequency (MHz)		difference
		calc.	obs.	
1	0	33·767	33·630	−0·147
2	−0·392	33·613	33·605	−0·008
3	−0·599	33·532	34·046	+0·514
4	−0·788	33·458	33·149	−0·309
5	+2·096	34·590	34·593	+0·003
6	+1·069	34·187	34·215	+0·028
7	+0·607	34·006	34·284	+0·278
8	+0·413	33·929	33·511	−0·418
9	+0·153	33·690	34·378	+0·688
10	−0·131	33·578	33·874	+0·296
11	+1·206	34·241	34·350	+0·109
12	+0·499	33·963	33·891	−0·052
13	+0·529	33·897	33·754	−0·143

While none of the deviations from equation (3) is outside the possible range of crystal field effects, it seems likely that in a series of compounds of such similar type deviations of 0·3 MHz or more are probably significant. Such deviations are observed in 3, 4, 8, and 9.

The effect of substituents on the Cl^{35} NQR frequency of chlorobenzene must arise from their influence on the CCl σ bond; for if they acted by altering the degree of π bonding between chlorine and the ring, the ρ constant in the corresponding Hammett relation would be negative, whereas the observed[5] value is +1·024 MHz. This conclusion is supported by a recent theoretical study[11] of Cl^{35} NQR chemical shifts in the chlorobenzenes which led to the conclusion that π bonding between chlorine and the ring is unimportant.* The fact that NQR chemical shifts obey the Hammett relation is then easily understood since the Hammett relation holds only in cases where specific resonance interactions are negligible.[12] Indeed, the Beidenknapp–Weiss[10] κ constants probably reflect the existence of such a "pure inductive" situation in chlorobenzene since standard σ constants, derived from the pK_A of substituted benzoic acids, are known to contain implicit allowances for specific resonance interactions in the case of p-substituents such as MeO or NH_2 that can undergo mutual conjugation with the carboxyl group.

If the NQR chemical shifts of substituted chlorobenzenes arose from inductive and/or field effects on the CCl σ bond, they should then also follow the Beidenknapp–Weiss relation. If, however, there is a significant hyperconjugative interaction of the

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* Arguments concerning the degree of π bonding in chlorobenzene based on the non-zero value of the asymmetry parameter of chlorine are not at all conclusive since it cannot be assumed that the asymmetry parameter reflects differences in population between the p AOs of chlorine; it could very well arise from asymmetric distributions of electrons on neighbouring atoms, in particular the adjacent carbon.

type symbolized in resonance terminology as participation by the ionic structure $(PhCH_2^+ Cl^-)$, one would expect deviations in the case of $-E$ or $-I$ substituents in positions *ortho* or *para* to chlorine, due to mutual conjugation, and one would also expect *ortho* substituents to exert a steric effect by reducing the conjugative interaction between chlorine and the ring. The latter point can be seen clearly from Fig 1. The hyperconjugative interaction in question arises from overlap between the CCl σ bond MO and the p AO of the adjacent carbon atom; this is most favoured in the indicated conformation (Fig 1a) where the CCCl plane is orthogonal to the ring and vanishes when the chlorine lies in the plane of the ring (Fig 1b). Steric repulsion between chlorine and a single *ortho* substituent will of course favour the latter conformation.
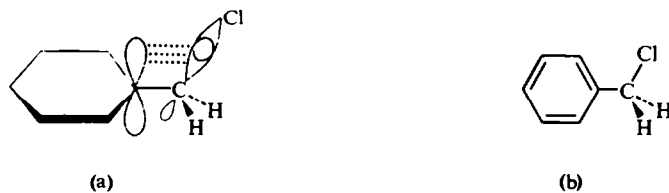

(a)   (b)

Fig 1. (a) Hyperconjugative interaction between phenyl and CCl in the favoured conformation of $PhCH_2Cl$; (b) Conformation in which the interaction vanishes.

Since the hyperconjugative interaction lowers the Cl^{35} NQR frequency, one would expect negative deviations from the Beidenknapp–Weiss relation in the case of $-I$ substituents (e.g. CH_3), or of $-E$ substituents (e.g. F, OMe) in the o, p positions, while the steric effect should lead to positive deviations in the case of single *ortho* substituents. The two largest deviations, both positive, in fact refer to compounds where there is a single *ortho* substituent (methyl in **3**, chloromethyl in **8**), while the other two large deviations, both negative, refer to compounds with $-E$ or $-I$ substituents, viz. *p*-fluorobenzyl chloride (**8**) and 2,4,6-trimethylbenzyl chloride (**4**). In **4** there are *two* ortho substituents so their effects cancel, the sterically favoured conformation being that of Fig 1a.

These observations suggest that resonance interactions do in fact lower the Cl^{35} resonance in **1** by an appreciable amount, probably of the order of 1 MHz. An obvious way to test this would be to study the Cl^{35} NQR spectrum of **24** where the chlorine atom necessarily lies in the plane of the benzene ring.

PhCHClPh

24   **25**   **26**
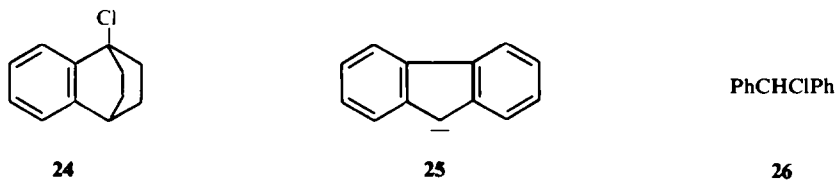
Allyl chloride is believed to exemplify a similar type of hyperconjugative interaction, its Cl^{35} NQR frequency (33·414 MHz[9]) being even less than that of benzyl chloride. Several derivatives were studied in the hope of elucidating this point; however, as so often, the project was foiled by failure of several of the compounds to give detectable signals. The very high frequency of the Cl^{35} resonance in chlorokojic acid (**20**) is, however, consistent with such a resonance interaction, this being suppressed in the case of **20** by the carbonyl group in the 3-position of the allyl chloride moiety.

Given the apparent importance of this type of allylic hyperconjugation, it occurred to us that 9-chlorofluorene (21) might be of interest. Fluorene is a much stronger acid than diphenylmethane because the central ring in the fluorenyl anion (25) is aromatic; the stability of this anion suggested that there should be less tendency for charge to migrate from the rings into the CCl bond in the case of 21 than in benzhydryl chloride (26). However the observed Cl^{35} NQR frequency for 25 (34·480 MHz) differed from that (34·36 MHz) reported for 26 by an insignificant amount.[13]

The PCl chlorine resonances in 22 and 23 (mean of crystal field doublets, 26·391 and 26·467 MHz) are close to the value (26·155 MHz) reported for PCl_3.[3] The corresponding value of the ring chlorine resonance in 23 (35·018 MHz) implies that PCl_2 in an electron-withdrawing group, its κ constant being $+0·323$ and its σ constant $+0·315$.

REFERENCES

[1] *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, Ohio (1970)
[2] R. Livingston, *J. Chem. Phys.* 19, 1434 (1951); B. P. Dailey, *Ibid.* 33, 1641 (1960)
[3] R. Livingston, *Ibid.* 57, 496 (1953)
[4] M. J. S. Dewar, M. L. Herr and A. P. Marchand, *Tetrahedron* 27, 2371 (1971)
[5] P. J. Bray and R. G. Barnes, *J. Chem. Phys.* 27, 551 (1957)
[6] G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instr.* 35, 698 (1964); 36, 702 (1965); 37, 1081 (1966)
[7] S. Saito, *J. Chem. Phys.* 36, 1397 (1962)
[8] D. H. McDaniel and H. C. Brown, *J. Org. Chem.* 23, 420 (1957)
[9] H. O. Hooper and P. J. Bray, *J. Chem. Phys.* 33, 334 (1960)
[10] D. Beidenknapp and A. Weiss, *Ibid.* 49, 3933 (1968)
[11] M. J. S. Dewar, G. E. Peterson and N. Trinajstić, work in course of publication.
[12] H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. Trav. Chim.* 78, 815 (1959)
[13] I. P. Biryukov, M. G. Voronkov and I. A. Safin, *Tabitsy Chastot Iadernogo Kuadrupalnogo Resonanza*, Izdatelystvoe "Khimiya" Leningradskoe Oldelenie (1968)