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DIPOLE MOMENTS AND ELECTRON DISTRIBUTION OF ACYL CHLORIDES AND ACYL BROMIDES

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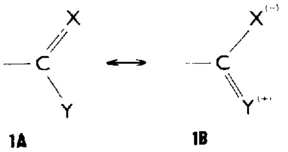
ABSTRACT

Dipole moments of *para*-substituted benzoyl chlorides and bromides, partly measured in benzene and partly recalculated from elderly literature, were analysed in terms of bond moments and additional contributions expressing the conjugation. Although the gross moments are similar, their decomposition yields different pictures for acyl chlorides and bromides. Only in the latter can significant electron transfer from the halogen be observed. On the other hand, conjugation with the benzene nucleus is strong in both aromatic acyl chlorides and bromides, but stronger in chlorides. There is agreement with the evidence from some other physical quantities but not from all.

Conjugation of a double bond with a lone electron pair has been studied most thoroughly on systems X=C(R)Y. Experimental proof was based on lengthening of the formally double bond C=X,[1-4] shortening of the formally single bond C—Y,[1-4] on their stretching frequencies[5] and on the barriers to rotation around the C—Y bond.[3,6] An independent line of evidence was obtained from dipole moments:[4,7-10] the vector difference (μ_m) of the actual dipole moment (μ_{exp}) and that calculated for the non-polar structure **1a** (μ_{calc}) may be interpreted as a charge redistribution originating from a contribution from the polar structure **1b** [equation (1)].

$$\mu_m = \mu_{exp} - \mu_{calc} \tag{1}$$



The absolute values of μ_m revealed[4,9] that conjugation generally increases with increasing basicity of Y (dialkylamides[7] > amides[7] > esters[8]), and less regularly also with the electron-attracting ability of X (amides > amidines,[4] but imidates ≈ esters[4]). To extend these

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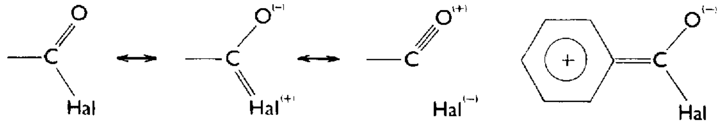
investigations to acyl halides (**2**) the possibilities are more restricted: no barrier to rotation exists and no x-ray structures are available except for an ester of chloroformic acid.[11] The object of this work was the analysis of the dipole moments of acyl chlorides (**3**, Table 1) and bromides (**4**) with some supporting arguments from published electron diffraction studies and *ab initio* calculations. From a comparison for the series amides[7]–esters[8]–acyl chlorides we expected that the contribution of structure **2b** would be reduced, almost negligible. In the study of chloroformates[11] we interpreted their dipole moments in terms of the formal no-bond structure **2c** rather than **2b**, but a more quantitative evaluation was hindered by the simultaneous presence of the alkoxy group.



2A **2B** **2C** **2D**

We processed the dipole moments of **3** and **4** in the same way as in our previous work.[4,7–10] First the direction of μ_{exp} was determined, exploiting the *para* substituents. Then μ_{calc} was obtained by vector addition of standard bond moments[12] of the bonds C=O and C—Cl or C—Br. Finally, μ_{m} was calculated according to equation (1). The merit of our procedure is treatment in terms of vectors, which even gives the direction of μ_{m}, compared with previous attempts on other classes of compounds[13] where the direction of μ_{m} was assumed *a priori*. Dipole moments of acyl chlorides **3a–d** were reported many years ago;[14] we recalculated them according to a more reliable procedure.[15].

EXPERIMENTAL

2-Methyl-5-nitrobenzoyl chloride,[16] m.p. 60 °C (chloroform) was used.

Substituted benzoyl bromides (**4a–4d**) were prepared from the sodium salts of carboxylic acids with phosphorous pentabromide,[17] purified by vacuum distillation or crystallization from carbon tetrachloride, kept over phosphorus pentoxide and used for measurement within 48 h. 2-Methyl-5-nitrobenzoyl bromide was prepared by the same procedure, m.p. 64 °C (hexane); found, C 39·04, H 2·65; calculated for $C_8H_6BrNO_3$, C 39·37, H 2·48%.

Dipole moments were determined in benzene solution by the method of Halverstadt and Kumler.[15] Solutions in benzene were prepared in a dry-box. Usually five different concentrations were used, not exceeding the weight fraction $w_2 = 0{\cdot}005$.

Relative permittivities of the solutions, ε_{12}, were measured at 25 °C on a heterodyne apparatus at a frequency of 1·2 MHz, the measuring cell being calibrated with specially purified benzene. Densities were measured with an Ostwald–Sprengel pycnometer.

Molar refractions, R_{D}, were calculated by summing Vogel's increments[18] valid for 20 °C, those for CO in ketones and for aliphatic chlorine or bromine being used throughout. For the substituents on the benzene ring, increments were used as derived directly from monosubstituted benzene derivatives, while the conjugation C_6H_5—CO was expressed by an additional increment of 1·3 cm^3. The latter correction accounts both for the conjugation within the functional group and for the conjugation with the benzene ring; the calculated R_{D} values for benzoyl chloride and bromide agree reasonably with the experimental values. Correction for atomic polarization was taken as 5% of the R_{D} value as recommended.[19] The results are listed in Table 1.

Table 1. Polarization and dipole moments of aroyl chlorides and bromides (benzene, 25 °C)

No.	Compound	α^a	β^a	P_2^0 ($cm^3 mol^{-1}$)	$R_D{}^b$ ($cm^3 mol^{-1}$)	μ^c (D)
3a	Benzoyl chloride[d]	9·36	−0·312	280·4	37·1	3·44
3b	4-Methylbenzoyl chloride[d]	11·28	−0·272	365·0	41·1	3·97
3c	4-Chlorobenzoyl chloride[d]	2·80	−0·401	129·8	42·0	2·05
3d	4-Bromobenzoyl chloride[d]	2·37	−0·529	137·8	44·9	2·11
3e	4-Nitrobenzoyl chloride[d]	0·919	−0·434	70·8	44·4	1·09
3f	3-Nitrobenzoyl chloride	8·06	−0·470	318·2	43·4	3·66
3g	2-Methyl-5-nitrobenzoyl chloride	8·15	−0·448	346·9	48·1	3·81
4a	Benzoyl bromide	6·11	−0·656	239·7	40·0	3·12
4b	4-Methylbenzoyl bromide	7·24	−0·541	306·9	44·6	3·57
4c	4-Chlorobenzoyl bromide	2·85	−0·524	158·1	44·9	2·33
4d	4-Bromobenzoyl bromide	2·88	−0·743	174·7	47·8	2·47
4e	2-Methyl-5-nitrobenzoyl bromide	7·24	−0·488	380·2	51·0	4·00

[a] Slopes of the plots ε_{12} and d_{12}^{-1}, respectively, versus the weight fraction w_2.
[b] Calculated from increments, see Experimental.
[c] Correction for the atomic polarization, 5% of the R_D value.
[d] Obtained by recalculating the original experimental data[14] according to the Halverstadt–Kumler procedure.[15] Several measurements at the highest concentrations have been omitted.

Theoretically expected dipole moments, μ_{calc}, were calculated by vector addition of standard bond moments[12] (in debye): $H-C_{al}$ 0·3, $H-C_{ar}$ 0, C=0 2·5, C—Cl 1·60, C—Br 1·57 (for halogens bonded on an sp^2 carbon) and $C_{ar}-NO_2$ 4·0. The bond angles used for the calculations, C—C=O 127° and C—C—Cl and C—C—Br 112°, were taken as means values from several electron diffraction and microwave studies.[20–23] The results of the calculations are shown in Figures 1 and 2.

RESULTS AND DISCUSSION

The first task is to determine the direction of the experimental dipole moments. In geometric terms this means constructing a triangle given its three sides: the dipole moments of the *para*-substituted compound, of the unsubstituted compound and of the substituent itself. When this triangulation was repeated for all *para*-substituted benzoyl chlorides (**3a–e**), good agreement

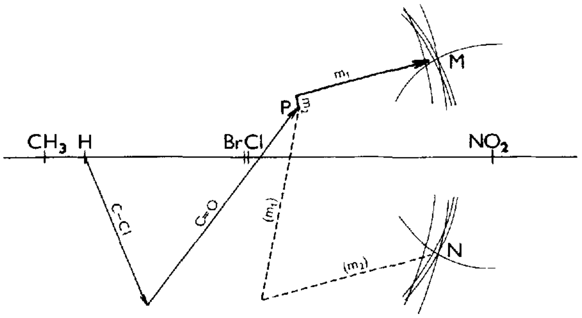


Figure 1. Vector analysis of dipole moments of aroyl chlorides **3a–3e**. Light arrows, bond moments; heavy arrows, mesomeric moments expressing the conjugation Cl—CO (**m**$_1$) and C_6H_5—CO (**m**$_2$); dotted lines rejected alternative

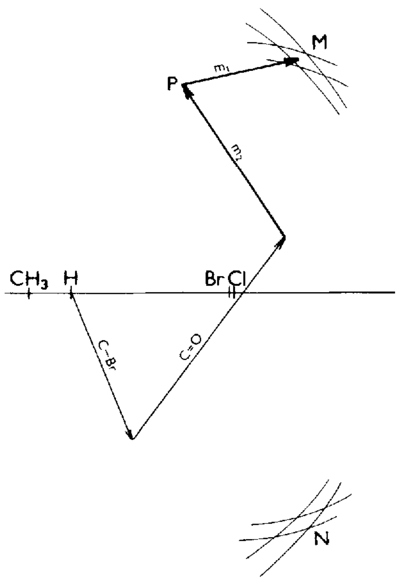


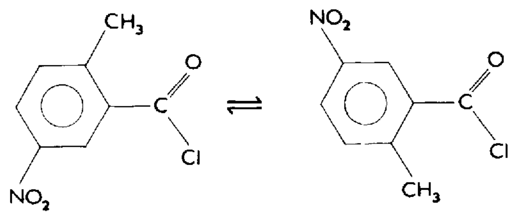
Figure 2. Vector analysis of dipole moments of aroyl bromides **4a–d**. Symbols as in Figure 1

was obtained (Figure 1). This agreement is proof of bond moment additivity on which our whole reasoning is based. It would be improved if the CH_3—C_{ar} dipole were taken as 0·4 D rather than 0·3 D as used hiterto,[12] but the improvement is not important. Note that there are in principle two solutions, the points M and N, of which M is preferred with regard to the subsequent analysis. The vector from H to M (not shown explicitly in Figure 1) represents the averaged group moment of the CCCl group; $\mu_{exp} = 3{\cdot}52$ D at an angle of 15° to the C_{ar}—C bond. In the next step, the expected dipole moment of the ideal structure **2a** (μ_{calc}) is obtained by summing the bond moments C=O and C—Cl in appropriate directions (vector from H to P). The difference μ_m [equation (1)] is represented by the vector from P to M and includes all interactions in the molecule of benzoyl chloride: in addition to those described by the structures **2b** and **c** (component denoted[7,8] $\mathbf{m}_2$), also the conjugation of the carbonyl bond with the benzene nucleus, structure **2d** (component $\mathbf{m}_1$). The latter can be estimated from the difference between the dipole moments of aliphatic and aromatic compounds:

$$\mathbf{m}_1 = \mu_{ar} - \mu_{al} + \mu(C_{al}\text{—}H) \qquad (2)$$

For μ_{al} the experimental value for acetyl chloride[24] (3·25 D in benzene solution) can be used. The direction of μ_{al} is not known but we can assume the direction of $\mathbf{m}_1$ from the centre of the benzene nucleus toward the oxygen atom, i.e. 12° to the C_{ar}—C bond. With this assumption, the solution of equation (2) is $\mathbf{m}_1 = 1{\cdot}37$ D (Figure 1) and $\mathbf{m}_2 = 0{\cdot}10$ is actually near to zero with respect to the inherent approximations. The dipole moment of acetyl chloride is then represented by a vector from the point CH_3 toward the point P (14° to the C—C bond, i.e. $-39°$ to the C=O bond). The latter value compares favourably with a determination[25] on formyl chloride ($-43°$) and also with calculated values[26,27] ($-39°$ and $-51°$, respectively). With the alternative direction of μ_{ar} (point N in Figure 1), an alternative solution of equation (2) would be obtained (dotted lines). However, this possibility can be rejected; on the one hand, the value of $\mathbf{m}_2$ would be inconceivably large (1·95 D), and on the other, the dipole moment of acetyl chloride would lie at an angle of -88° to the C=O bond, at variance with the above results for formyl chloride.[25-27] All the available evidence, both experimental[25,28] and theoretical,[26,27] suggests that the dipole moments of acyl chlorides are situated nearer to the C=O than to the C—Hal bond. The same holds for acyl fluorides;[26,27,29-31] the most recent calculation on formyl fluoride[32] (STO 631G) yielded $\mu = 2{\cdot}753$ D, 42° to the C=O bond.

We attempt to obtain further experimental proof using 2-methyl-5-nitrobenzoyl chloride (**3g**). There are good grounds[33] for believing that its conformation is planar and the form **3gA** should be more populated than **3gB** for steric reasons. Then the alternative M would require that the experimental value of μ^2 is nearer to the lower of the two calculated values. Contrary to expectation, the conformation **3gA** is only 40% populated. The steric hindrance of the methyl group is negligible since we obtained almost the same conformational equilibrium (36%) for simple 3-nitrobenzoyl chloride (**3f**).



3g (A) **3g(B)**

$\mu_{\text{calc}} = 2{\cdot}69$ D (40%) $\mu_{\text{calc}} = 4{\cdot}39$ D (60%)

From the preceding analysis it follows that there is little conjugation, if any, within the COCl group, but in aromatic derivatives this group is strongly conjugated with the benzene nucleus. The latter conjugation is expressed by a vector $\mathbf{m}_1 = 1{\cdot}37$ D, whereas in esters,[8] dimethylamides[7] and thiol esters[34] it does not exceed 0·3 D, as follows directly from comparison the dipole moments[24] of corresponding derivatives of acetic and benzoic acid. On the other hand, the determination of the COCl conjugation ($\mathbf{m}_2 = 0{\cdot}10$, or almost zero) did not follow only from experimental facts but depends also on the assumption about the direction of $\mathbf{m}_1$ (Figure 1). In previous work[7,8,11,34,35] the latter was assumed in the C_{ar}—C bond instead of from the ring centre toward O as here. This choice was without consequence in the case of small values,[7,8,34,35] but it could affect the present results, giving rise to $\mathbf{m}_2$ up to 0·5 D (see Figure 1). In the belief that the COCl conjugation is actually negligible, we searched for arguments from other physical quantities.

Chlorine quadrupole coupling constants in acetyl chloride[36] and propionyl chloride[37] were interpeted by a 9 or 10% π-character (from the structure **2b**) and 42 or 36% ionic character of the C—Cl bond. The integrated absorption intensity A(C=O) in acetyl chloride suggests a conjugation similar to that in esters but much weaker than in amides.[38] The intensity of ring vibrations $A(\nu_{16a} + \nu_{16b})$ reveals a much stronger conjugation with the benzene ring than in esters or amides,[38] this is confirmed also from the barriers to rotation around the C_{ar}—C bond.[39] From electron diffraction and microwave determinations on acyl chlorides without electron-attracting substituents,[20-22,28,40-43] we obtained average values $l(\mathrm{C{=}O}) = 1{\cdot}19_0$ and $l(\mathrm{C{-}Cl}) = 1{\cdot}79_3$ Å. The former is insignificantly shorter than in esters[1] and the latter is almost equal to that in primary chloroalkanes but longer than that in chloroalkenes.[44] We were unable to find any mutual dependence of these two bond lengths, as is observed, for example, in esters[1] or amidines.[4] Moreover, there was no difference between conjugated[22,28,40–42] and non-conjugated[20,21,44] acyl chlorides; only derivatives with electron-attracting substituents[45–48] showed a shortened C—Cl bond. More significant is the shortening of the C_{ar}—C(O) bond in aromatic acyl chlorides,[22,40] suggesting a stronger conjugation than in aromatic esters.[1] The heat of formation of acetyl chloride[49] enabled us to construct an isodesmic (in the broader sense) reaction [equation (3)], whose reaction enthalpy is only a quarter of the value for acetic acid[50] or methyl acetate (−79 kJ).

$$(CH_3)_2CHHal + (CH_3)_2C{=}O \rightarrow CH_3C(O)Hal + (CH_3)_3CH \tag{3}$$

$$\text{Hal} = \text{Cl: } H^0_{298} = -22 \text{ kJ mol}^{-1}$$

$$\text{Hal} = \text{Br: } H^0_{298} = -16 \text{ kJ mol}^{-1}$$

All these molecules are stabilized, but part of the stabilization energy may be due to factors other than conjugation. Of similar compounds, imidoyl chlorides[51] did not reveal any conjugation. In chloroformates a complex interaction was found[11] that was not present in acyl chlorides or esters; our conclusion about the similarity of chloroformates an acyl chlorides was based on the wrong vector direction in the latter, now disproved. Most recently the strong conjugation with the benzene ring in benzoyl chloride was inferred from ^{17}O NMR shifts.[52]

When the whole analysis was repeated for benzoyl bromides (**4a–d**) a quantitatively different result was obtained (Figure 2). The gross moments of **3** and **4** are similar but the moment of the COBr group (3·20 D) differs from that of COCl mainly in its direction (± 45° to the C_{ar}—C bond). Similarly as for acyl chlorides, we preferred the vector direction from P to M on the basis of equation (2) and of the experimental dipole moment of acetyl bromide[24] (2·45 D). In the present case the decision was unambiguous since the equation has no solution for the alternative direction (from P toward N). Similarly to **3g**, **4e** did not help in deciding between the two directions. Its conformation, similar to **3gA**, is 47% populated only; evidently even the steric hindrance of bromine is insufficient. As the final result we obtained the vector $\mathbf{m}_1 = 1{\cdot}20$ D, corresponding to a weaker conjugation with the benzene ring (**2d**) than in acyl chlorides, and a surprisingly large value of $\mathbf{m}_2 = 1{\cdot}80$ D (124° to the C_{ar}—D bond). With respect to its direction, the latter value should not be interpreted as a contribution of the structure **2b** but rather as reduced polarization of the C—Br bond.

It is true that the experimental dipole moments of **4** are loaded with larger errors than usual, owing to the instability of the samples. Also, the fit in Figure 2 is worse than that in Figure 1 and the important 4-nitro derivative is lacking because the compound was insufficiently soluble. Although the value of $\mathbf{m}_2$ may be overestimated, we believe that the difference in the charge distribution in acyl bromides and chlorides is real. Evidence from other physical properties is scarce. The C=O bond length in several acyl bromides[20,23,45] is insignificantly shortened compared with structurally similar chlorides. However, the C—Br bond length[20,23], $1{\cdot}96_7$ Å, is not only longer than that in bromoalkenes but even than in bromoalkanes.[44] Of the infrared intensities,[38] A(C—O) indicates a stronger interaction in bromides but $A(\nu_{16a} + \nu_{16b})$ also suggests a stronger conjugation with the benzene ring. In contrast, the rotational barrier is lower in benzoyl bromide.[39] The reaction enthalpy of the isodesmic reaction (3) suggests again a stronger interaction in acetyl bromide which, of course, can have a different basis. Even the molar refraction yields an accordant picture, although it is controlled also by the properties of the excited state. The experimental values for acetyl chloride and bromide are 0.7 and 1.0 cm^3, respectively, larger than those calculated from increments;[18] benzoyl chloride and bromide reveal an additional increase of 0.6 and 0.2 cm^3.

In conclusion, there is some evidence that the interaction in the molecule of acyl bromides is stronger than that in acyl chlorides, but the result from dipole moments is the most salient. Verification by another method seems desirable.

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