Circular Dichroism Studies of Aromatic Acid Chlorides

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Summary The isotropic absorption and c.d. spectra of (1*S*,2*S*)-(+)-*trans*-2-phenylcyclohexanecarbonyl chloride (**1**) and (*R*)-(−)-α-methoxyphenylacetyl chloride (**2**) are reported and the band in the 245—250 nm region assigned to the *n*–π* transition of the chlorocarbonyl chromophore.

THE lowest energy electronic transition of the carboxy-group occurs in the 205—210 nm region.[1] Replacement of the hydroxy-group by chlorine results in a bathochromic shift of *ca.* 35 nm (Table 1). The available data, although

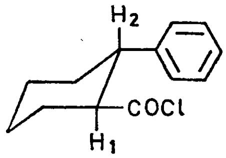
TABLE 1. *U.v. maxima of some aliphatic acids and acid chlorides*

Compound	Solvent	λ_{max}/nm	$\epsilon_{max}/M^{-1}\,cm^{-1}$
$MeCO_2H$[a]	95% Ethanol	204	41
MeCOCl[b]	Heptane	240	34·5
cyclo-$C_6H_{11}CO_2H$[c]	95% Ethanol	212	67
cyclo-$C_6H_{11}COCl$[c]	Heptane	245	72

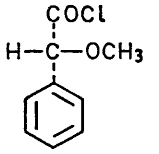
[a] H. Ley and B. Arends, *Z. Physik. Chem.*, 1932, **B17**, 177.
[b] B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, 1951, **19**, 994.
[c] This work.

very limited (particularly for the acid chlorides), support the identification of these bands for both chromophores as n–π^* transitions.[2]

Chiroptical data on optically active acid chlorides have been lacking. We present the results of c.d. studies of two aromatic acid chlorides (+)-(**1**) and (−)-(**2**).†



(1)



(2)

The chemical shifts and band widths of the H¹ and H² protons of (**1**) (H^1 $\delta = 3{\cdot}0$ p.p.m., band width = 25 Hz; $\delta = 2{\cdot}8$ p.p.m., band width = 25 Hz) were determined at 100 MHz. The broad band widths are as expected for axial protons owing to the large J_{ax-ax} in the cyclohexane series.[3] Low-temperature n.m.r. measurements showed no change in the chemical shifts or band widths, thus confirming the deductions from conformational free-energy considerations and examination of Corey–Pauling space-filling molecular models, namely, that (**1**) exists almost exclusively in the equatorial-phenyl conformation.

N.m.r. studies of (**2**) cannot give conformational information since the methoxy and methine protons both give singlets. However, the carboxylic acid corresponding to (**2**) has been reported to be a conformationally mobile homoconjugated system.[4]

The isotropic u.v. and c.d. spectra of both the acid chlorides are presented in Figures 1 and 2, respectively.

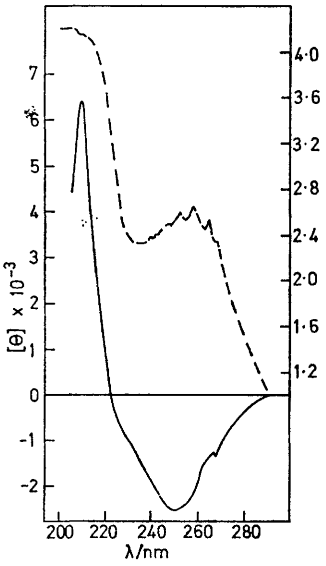


FIGURE 1. *Isotropic absorption (dashed curve) and c.d. (solid curve) spectra of* (1S,2S)-(+)-trans-2-*phenylcyclohexanecarbonyl chloride in heptane.*

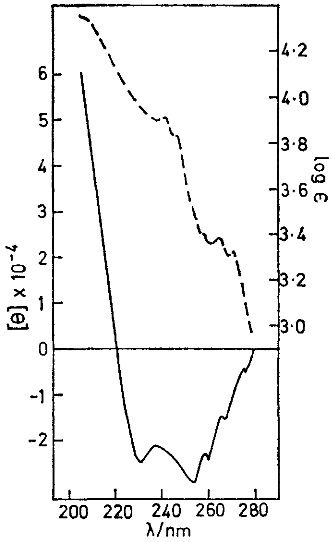


FIGURE 2. *Isotropic absorption (dashed curve) and c.d. (solid curve) spectra of* (R)-(−)-α-*methoxyphenylacetyl chloride in heptane.*

TABLE 2 *C.d. maxima in heptane at* 27°

Compound	λ/nm ([θ]/deg cm² dmol⁻¹)		
(+)-(**1**)	209·5 (+6400)	251 (−2500)	268 (−1300)
(−)-(**2**)	231 (−25000)	254 (−29000)	260 (−24000)
	268 (−15000)	277 (−4500)	

C.d. data are given in Table 2. The u.v. spectral features are similar to those reported for aromatic carboxylic acid derivatives,[5] exhibiting the vibrational structure of the ^1L_b phenyl transition in the 260 nm region with the much more intense ^1L_a aromatic transition seen as a shoulder near 210 nm. However, in contrast to the aromatic carboxylic acids, a third band occurs near 245 nm in the u.v. spectra of the acid chlorides. The band, whose vibrational structure is more clearly resolved in the spectrum of (**2**) is assigned to the n–π^* transition of the chlorocarbonyl group.

The c.d. spectrum of (+)-(**1**) contains a broad negative band centred at 251 nm, which overlaps and almost completely obscures the ^1L_b Cotton effect in the 260 nm region. The width at half-height of this band, 35 nm, is similar to that for simple carboxylic acids and esters.[6] The available evidence leads us to assign the 251 nm Cotton effect to the n–π^* transition of the chlorocarbonyl group. This band is overlapped on the short wavelength side by a more intense Cotton effect at 209·5 nm due to the ^1L_a transition of the phenyl chromophore. The much narrower half-height band width (*ca.* 20 nm) is similar to the ^1L_a aromatic Cotton effects reported recently by Craig and his co-workers.[7]

The c.d. curve of (−)-(**2**) (Figure 2) exhibits many of the features found for (+)-(**1**), although the ellipticity values are about an order of magnitude more intense. A broad negative band is found in the 225—275 nm region with a more intense Cotton effect overlapping it at shorter wavelength. However, a feature not observed in the c.d. of (+)-(**1**) is the presence of *two* negative maxima at 254 and 231 nm. The 254 nm peak is not considered to be due to the ^1L_b transition since its intensity is *ca.* 100 times that found for the corresponding carboxylic acid,[4] and more

† Satisfactory elemental analyses were obtained for these compounds.

than twice as large as reported for the ^1L_b band of (−)-*trans*-2-phenylcyclopropanecarboxylic acid,[8] a highly coupled system. This Cotton effect is only slightly shifted from the n–π^* band observed in the corresponding isotropic absorption spectrum and it is assigned to the same transition. The origin of the 231 nm Cotton effect remains, as yet, not determined. If, in this conformationally mobile system, the band arises from the n–π^* transition of another significantly populated conformer, then the Cotton effect of opposite sign observed below 215 nm must be due to the ^1L_a aromatic transition. The resolution of this question awaits the results of further work on the chlorocarbonyl chromophore.

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