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THE INTRAMOLECULAR NH···Cl HYDROGEN BOND IN UREA DERIVATIVES CONTAINING THE *o*-CHLOROPHENYL GROUP

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ABSTRACT

The solution ν(N—H) vibrations of various disubstituted ureas containing a halophenyl group have been examined in order to directly confirm the presence of an intramolecular NH···Cl hydrogen bond in the *o*-chloro analog. In chlorophenyl derivatives the ν(N—H) band for the N—H bond adjacent to an *o*-chlorophenyl group is always lower than that for a N—H bond adjacent to a phenyl, *m*- or *p*-chlorophenyl group. The corresponding band in *N*-*o*-halophenyl-*N'*-phenylureas, *o*-XPhUPh [U = HNC(O)NH], shifts to significantly lower wavenumber with increasing atomic size or weight of halogen. The *o*-XPhUPh derivatives are concluded to be in two intramolecularly NH···X hydrogen-bonded forms with N—H *trans* or *cis* to the C=O group.

INTRODUCTION

A lowering in the ν(N—H) wavenumber for the *o*-chlorophenyl (*o*-Cl) analog of R_2UPhCl type ureas in solution was concluded to be due to intramolecular NH···Cl hydrogen-bond formation [1]. This was supported by the following: (a) no associated ν(N—H) bands for the *o*-Cl analog appear, even in saturated solution; (b) the monomeric ν(N—H) band is stronger and sharper than those of the other analogs; (c) some of the *o*-Cl analogs exhibit a sharp ν(N—H) band in the solid state within ca. 10 cm^{-1} of the ν(N—H) band position in solution.

As a continuation of this work the IR spectra of *N*,*N'*-dichlorophenylureas (ClPhUPhCl) and *N*-halophenyl-*N'*-phenylureas (XPhUPh) have been studied in solution in the ν(N—H) region. The purpose of this study is to directly confirm intramolecular NH···Cl hydrogen-bond formation by determining whether or not the ν(N—H) band due to the N—H bond adjacent to an *o*-halophenyl (*o*-XPh) group shifts to lower wavenumber with increasing atomic size or weight of halogen. No IR data have as yet been reported for urea derivatives containing XPh groups.

EXPERIMENTAL

The compounds ClPhUPhCl and XPhUPh were synthesized by adding chlorophenyl isocyanate and phenyl isocyanate to the corresponding chloroanilines and haloanilines, respectively. Solid reagents were used as ethanol solutions. Crude samples were purified through repeated recrystallization from suitable solvents. Solutions ($\leqslant 1.0 \times 10^{-3}$ M) prepared using spectral grade CCl_4 were studied by IR spectroscopy. The spectrometer experimental conditions, calibration of band positions and wavenumber accuracy were the same as described previously [2].

RESULTS AND DISCUSSION

ν(N—H) bands and conformations of ClPhUPhCl

Two fundamental ν(N—H) bands from two N—H bonds should appear in the IR spectra of *N*, *N*′-disubstituted ureas (RUR′) assuming that there is no rotational isomerism. Considering that the steric effect, *ortho* effect, etc. of substituents probably influence the ν(N—H) vibrations, chlorophenyl (ClPh) groups for R and R′ of RUR′ were chosen as shown in Table 1.

A number of ClPhUPhCl derivatives exhibit two ν(N—H) bands, as expected or one band having two overlapping components. Exceptions are *o*-ClPhUPh and the three Cl_2PhUPh isomers which show three ν(N—H) bands. Taking into account ν(N—H) band positions and substituents, the observed bands can be classified into three groups: A, B and C [A: Ph, *m*-ClPh and *p*-ClPh, 3432—3437; B: *o*-ClPh and three Cl_2Ph, 3408—3418, *o*-ClPh and 2,4-Cl_2Ph, 3412—3418, 2,5- and 2,6-Cl_2Ph, 3408—3412; C: *o*-ClPhUPh and three Cl_2-PhUPh, 3396—3401 cm^{-1}]. In the B bands it appears that two chlorine atoms of the dichlorophenyl (Cl_2Ph) groups have at least as much effect as the *o*-chlorine atom of the *o*-ClPh group from steric and geometric points of view.

The following features suggest that bands A and B arise from the conformations with N—H *trans* to C=O, without and with an intramolecular NH···Cl hydrogen bond respectively, and that band C is due to the conformation

TABLE 1

Observed ν(N—H) wavenumbers (cm^{-1}) for dichlorophenylureas, RNHC(O)NHR′, in CCl_4

R[a]	R′								
	Ph			*o*-ClPh		*m*-ClPh		*p*-ClPh	
	A	B	C	A	B	A	B	A	B
o-ClPh	3432	3415	3401		3415	3434	3414	3437	34
m-ClPh	3442, 3427			3434	3414			3440, 3426	
p-ClPh	3441, 3427			3437	3414	3440, 3426			
2,6-Cl_2Ph	3437	3411	3399		3414, 3410	3432	3409	3433	34
2,5-Cl_2Ph	3436	3412	3396		3417	3436	3412	3435	34
2,4-Cl_2Ph	3432	3417	3399		3418	3436	3415	3434	3

[a] For R = R′ = Ph (PhUPh) bands are observed at 3441 and 3427 cm^{-1}.

with N—H *cis* to C=O. (1) Bands A, B and C correspond to the *trans* N—H band without and with the intramolecular NH···Cl hydrogen bond, and to the *cis* N—H band of R_2UPhCl, respectively [1]. However, each of the band positions is systematically lower by ca. 25 cm^{-1} than the corresponding bands of R_2UPhCl. That the *trans* bands of *N*, *N'*-dialkylsubstituted ureas RHNC(O)NHR=RUR [3] are lower by ca. 25 cm^{-1} than the corresponding bands of trialkylsubstituted species was reported earlier [4]. (2) A comparison of ν(N—H) data for *N*-alkyl-*N'*-phenylureas (RUPh) in Table 2 with those for RUR [3] indicates that the bands near 3440 cm^{-1} are assignable to the *trans* ν(N—H) mode for the N—H bond adjacent to a Ph group.

There are three possible combinations of the A and B bands; A—A, A—B and B—B. In the A—A combination, e.g. in *m*-ClPhUPh, two components which do not overlap are split by resonance to give two bands at 3427 and 3442 cm^{-1}, outside the above defined regions. The band at 3427 cm^{-1} is about twice as strong as that at 3442 cm^{-1}. *N*, *N'*-Diphenylurea (PhUPh) also shows these two bands, suggesting that in solution PhUPh is in the *trans-trans* form with C_s symmetry. Although it has been reported that the two bands of PhUPh arise from the *trans* and the *cis* forms [5], the band at lower wavenumber being ascribed to the *cis* form [6], this interpretation is incorrect. The A—B and B—B combinations give rise to two bands and a band comprising two overlapping components within the above defined regions, respectively.

TABLE 2

Observed ν(N—H) wavenumbers (cm^{-1}) for RUPh and RTUPh in CCl_4

R	RNHC(O)NHPh (RUPh)	R = R' (RUR)	RNHC(S)NHPh (RTUPh)	R = R' (RTUR)
CH_3	3458, 3436	3461	3413	3445
C_2H_5	3444, 3437[a]	3449	3417, 3401	3435
n-C_3H_7	3446, 3435	3453	3416, 3405[a]	3435
iso-C_3H_7	3434, 3440	3437	3417, 3388	3422
n-C_4H_9	3444, 3438	3450		
iso-C_4H_9	3447[a], 3438	3455	3414, 3407	3439
sec-C_4H_9	3435, 3440	3438	3416, 3386	3421
tert-C_4H_9	3432, 3440	3437	3410, 3383	3418
Assignment	R Ph	[3]	Ph R[b]	[8]

[a] Shoulder. [b] The ν(N—H) band for the N—H bond adjacent to an alkyl group for RTUPh appears at a wavenumber lower by 30—35 cm^{-1} than the corresponding band for RTUR. This suggests that the N—H bond is *cis* to the C=S group. The same results were reported for MeTUPh, Bu^iTUPh. Bu^sTUPh and Bu^tTUPh, W. Walter and K. P. Rueß, Liebigs Ann. Chem., 746 (1971) 54.

o-XPhUPh and the intramolecular NH···Cl hydrogen bond

In order to directly confirm intramolecular NH···Cl hydrogen-bond formation in the *o*-Cl analogs of R_2UPhCl and ClPhUPhCl, the shifts of ν(N—H) bands due to halogen exchange were examined for some derivatives of *o*-halophenylureas (*o*-XPhUR'; R' = Ph, Me and Et) in solution. The observed ν(N—H) wavenumbers are summarized in Table 3 together with those of *p*-substituted analogs as references.

First, the ν(N—H) data for ClPhUPh are compared with those for XPhUPh. As mentioned above, *o*-ClPhUPh gives rise to two bands of the A and B type at 3432 and 3416 cm^{-1} due to the *trans* form and a band of C type at 3401 cm^{-1} due to the *cis* form, while *p*-ClPhUPh shows two A—A combination bands at 3441 and 3427 cm^{-1} due to the *trans* form.

The other *o*-XPhUPh derivatives also exhibit three bands; one at a constant position exactly similar to the A band and two shifting from the B and C band positions of *o*-ClPhUPh. These latter two bands shift to lower wavenumber with increasing atomic size or weight of halogen, as can be seen in Fig. 1(a). The other *p*-XPhUPh derivatives show two bands at positions very similar to those of *p*-ClPhUPh.

The two band-shiftings of the *o*-analog caused by the exchange of halogen atom conclusively suggest that the intramolecular hydrogen bond is formed between the N—H group and the *o*-halogen atom, as is well known in *o*-halophenols [7], and that *o*-XPhUPh derivatives in solution exist in two *trans* forms and one *cis* form. The bands which remain constant originate from PhNH and *p*-XPhNH structures, in which the halogen atom is far away from the N—H group.

Second, the ν(N—H) data for XPhUPh are compared with those for XPhUMe and XPhUEt. From the ν(N—H) data for RUPh summarized in

TABLE 3

Observed ν(N—H) wavenumbers (cm^{-1}) for XPhUR' in CCl_4

R	RNHC(O)NHR'			RNHC(S)NHR'
	R' = Ph (XPhUPh)	R' = Me (XPhUMe)	R' = Et (XPhUEt)	R' = Ph (XPhTUPh)
o-FPh	3430, 3443, 3430	3461, 3443	3449	3409, 3380
o-ClPh	3432, 3415, 3401	3459, 3418	3445, 3419	3410, 3379, 3346
o-BrPh	3430, 3403, 3387	3461, 3408	3446, 3407	3410, 3381, 3330
o-IPh	3429, 3386, 3368	3459, 3393	3444, 3391	3411, 3381, 3307
p-FPh	3442, 3428	3458, 3435	—	3413, 3382
p-ClPh	3441, 3427	3459, 3437	3444	3408, 3377
p-BrPh	3441, 3426	3459, 3437	3445	3412, 3381
p-IPh	3440, 3427	3459, 3437	3445	3409, 3379
Assignment	Ph XPh	Me XPh	Et XPh	Ph XPh

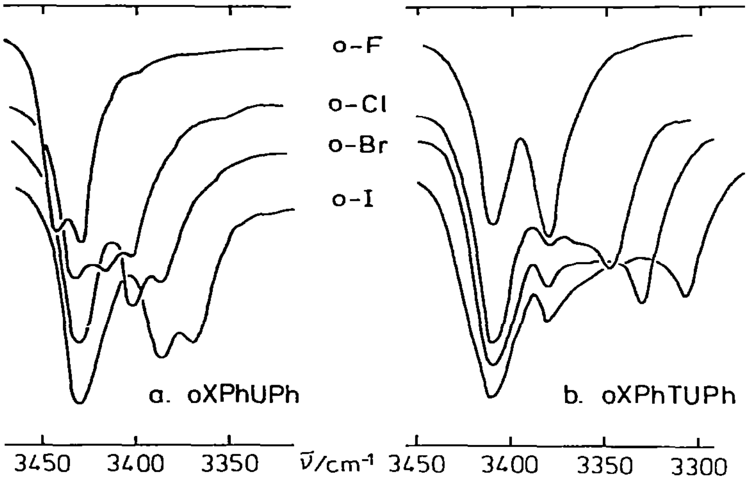

Fig. 1. IR spectra in the ν(N—H) region of *N*-*o*-halophenyl-*N*'-phenyl-ureas (a) and -thioureas (b) in CCl_4.

Table 2, the band due to the *trans* N—H bond adjacent to the Me or Et group is expected to appear near 3458 or 3444 cm^{-1}, respectively. The compound XPhUMe exhibits one band in the range 3458—3461 cm^{-1} due to the N—H bond adjacent to the Me group and another band, which shifts from 3343 (*o*-F analog) to 3393 cm^{-1} (*o*-I analog) for the *o*-X analog and remains constant within 3435—3437 cm^{-1} for the *p*-X analog, due to the N—H bond adjacent to the XPh group. The compound *p*-XPhUEt shows a band in the range 3444—3449 cm^{-1}, which comprises two overlapping components due to N—H bonds adjacent to Et and *p*-XPh groups. The compound *o*-XPhUEt shows one band at a constant position due to the N—H bond adjacent to Et group and another band shifting from 3449 cm^{-1} (*o*-F analog) to 3391 cm^{-1} (*o*-I analog) due to the N—H bond adjacent to an *o*-XPh group.

The shifting bands of *o*-XPhUMe and *o*-XPhUEt are similar in wavenumber to the corresponding bands of *o*-XPhUPh to the B *trans* band of *o*-ClPhUPh. These bands arise from the intramolecularly hydrogen-bonded *trans* form.

Finally, the ν(N—H) bands of XPhTUPh [TU = HNC(S)NH] are considered. From the ν(N—H) data for RTUPh summarized in Table 2, the band due to the *trans* N—H bond adjacent to the Ph group of XPhTUPh is expected to appear near 3410—3417 cm^{-1}. If the ν(N—H) wavenumber differences of 13—16 cm^{-1} between *N*, *N*'-di- and tri-alkylthioureas with the same alkyl groups [2] are applicable in this case, then the ν(N—H) band positions for the *trans* and the *cis* form of XPhTUPh could be predicted from the data for R_2TU(*p*-ClPh) [1] and R_2TUPh [9]. The ν(N—H) band due to the N—H bond adjacent to the XPh or Ph group of XPhTUPh where there is no hydrogen-bond formation is expected to appear near 3415—3420 cm^{-1} for the *trans* form and near 3371—3376 cm^{-1} for the *cis* form.

In the spectra of XPhTUPh, both *o*-X and *p*-X analogs show two bands at ca. 3410 and 3380 cm^{-1} and in addition the *o*-X analog shows one band shifting from 3380 cm^{-1} (*o*-F analog) to 3307 cm^{-1} (*o*-I analog), as shown in Fig. 1(b). It is reasonable that in the *o*-X analog, the lower of the two non-shifting bands and the shifting band have the same origin since the intensities of these bands are about half of that of the higher non-shifting band, as shown in Fig. 1(b), while in the *p*-X analog the two bands have a similar intensity.

It is concluded that the higher band arises from the *trans* N—H bond adjacent to the Ph group and the lower band from the *cis* N—H bond adjacent to the XPh group, neither involving any intramolecular hydrogen bond. The shifting bands are due to the intramolecularly hydrogen-bonded *cis* form of the N—H bond adjacent to the *o*-XPh group. The fact that the non-hydrogen-bond *cis* bands of the *o*-X and *p*-X analogs appear at very similar positions to each other indicates that the steric effects of *o*- and *p*-chlorine atoms on the N—H bonds are not distinguishable.

In all urea derivatives with *o*-XPh groups, the N—H bond adjacent to this group can be *trans* and *cis* related to the C=O group when there is an intramolecular NH···X hydrogen bond. In thiourea derivatives with *o*-XPh groups, on the other hand, it is in the *cis* position relative to C=S with and without the intramolecular hydrogen bond. The existence of non-hydrogen-bonded N—H and the absence of N—H *trans* to C=S in the latter may be due to the lower resonance contribution of the lower electronegativity and the larger steric effect of the sulfur atom on this bond relative to that of the oxygen atom, respectively. However, it is strange that *o*-ClPhU(*o*-ClPh), *o*-ClPhU(*p*-ClPh), etc. exhibit no *cis* ν(N—H) bands. It is clear that no Ph—Ph stacking interaction takes place in *N*, *N'*-disubstituted ureas with two aryl groups.

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