2704 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2704—2707 (1975) [Vol. 48, No. 10

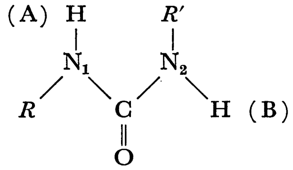
The Steric Effects of Alkyl Groups on the N–H Stretching Vibrations and the Rotational Isomerism of Alkylureas

Yoshiyuki Mido and Tamotsu Gohda
Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657

(Received April 14, 1975)

The free N–H stretching vibrations of various trialkylureas, R_2UR', in dilute solutions were studied in order to resolve our questions concerning the rotational isomerism of dialkylureas. In the infrared spectrum of R_2UR', where R is isopropyl or cyclohexyl, an additional N–H band appears on the higher-frequency side of the *trans* N–H band. It was also observed that the larger the effective size of the R' group on R_2UR' is, the stronger the intensity of the additional band becomes. It was concluded, in connection with the rotational isomerism of dialkylureas, that the additional band arises from a form in which the N–H group is out of the skeletal plane.

In our previous studies of mono- and dialkylureas,[1–4] it was shown that *N,N'*-dialkylureas (RUR') in solution take the configuration with the *trans-trans* relation between the C=O group and the two N–H groups; this was contrary to the interpretation by Rao *et al.*[5] However, the infrared spectrum of *sym*-di-*t*-butylurea (*s*-D*t*BU) showed a very weak N–H stretching band (3469 cm^{-1}) in addition to the *trans* N–H stretching band (3437 cm^{-1}); this suggested that the coexistence of a certain additional isomer arises as a result of the steric hindrance between the bulky alkyl group and the C=O group.[1] If this isomer, coexisting with the dominant *trans-trans* isomer, is assumed to be in the *trans-cis* configuration, the substitution of another bulky group for either of the two imino hydrogen atoms on RUR' having bulky groups will stabilize the *trans* form further for the following reasons.



trans-cis

The substitution of the bulky group at the A site may decrease the amount of the *cis* form about the C–N$_2$ axis by virtue of the steric hindrance between the substituted group and the R' group. On the other hand, the substitution at the B site does not change the *trans* form about the C–N$_1$ axis. Accordingly, in the spectra of trialkylureas with bulky groups, the band corresponding to the 3469 cm^{-1} band of *s*-D*t*BU is expected to be weak or absent, if the above assumption is correct.

Thus, in the present study, the N–H stretching vibrations of various trialkylureas, $R_2NCONHR'$ (R_2UR'), were investigated in order to examine whether or not the 3469 cm^{-1} band of *s*-D*t*BU arises from the *cis* form and to establish the relationships between the configurations and the N–H stretching frequencies of R_2UR'.

Experimental

Various R_2UR' substances were prepared by adding the corresponding alkylisocyanate to some dialkylamines. These crude samples were purified by repeated recrystallizations from suitable solvents, and the purified samples were identified by elementary analysis. Solvents for spectroscopy were used.

The infrared measurements were made with a Hitachi EPI-2G Infrared Grating Spectrophotometer. Samples were examined as 0.02 M solutions using 5-mm (3 μm region) and 0.5-mm cells (6 μm region). The recording conditions of the spectra were the same as in the previous study.[1]

Results and Discussion

The N–H Stretching Bands. The infrared spectra of R_2UR' in solutions will exhibit only one free N–H stretching band, if rotational isomerism is not taken into account, since R_2UR' substances have only one N–H bond. However, as is shown in Table 1 and Fig. 1, where the observed free N–H stretching bands are summarized, the spectra of ten R_2UR' derivatives (five D*i*PUR' and five DcHUR') exhibited two free N–H bands (we will conventionally denote this type of R_2UR' as R_2UR'-II), and the spectra of the other R_2UR' derivatives showed one free N–H band (R_2UR'-I). Also, cHMUR'-type compounds, examined for comparison, exhibited only one N–H band (see the bottom of Table 1). Among the three kinds of solutions studied, the CS$_2$ solution showed most prominently the two N–H bands of R_2UR'-II.

From the comparisons of the band positions, the lower-frequency band of R_2UR'-II, as well as only one band of R_2UR'-I and cHMUR', is assigned to the N–H stretching vibration arising from the configuration with the *trans* relation between the N–H and C=O groups.

These N–H bands—the band of R_2UR'-I and the lower band of R_2UR'-II—appear at the positions characteristic of the substituent, R', attached to the N–H bond. Such correlations between the N–H stretching frequencies and the type of R' group correspond to the similar correlations obtained previously for the *trans* N–H stretching frequencies of RUR',[1–4] although the N–H frequencies of R_2UR' are higher by ~20 cm^{-1} than those of the *trans* bands of RUR'.

On the other hand, the spectra of R_2UR'-II showed another free N–H band observed at the higher-(approximately 20 cm^{-1}) frequency side of the *trans* N–H band. As may be seen from Table 1, the appearance of the two free N–H bands is dependent upon the bulkiness of the R groups on R_2UR' but not on that

Table 1. The N-H stretching frequencies (cm^{-1}) of R_2NCONHR'

R_2	Solvent	R' M (methyl)	E (ethyl)	iP (isopropyl)	cH (cyclohexyl)	tB (t-butyl)
DM (dimethyl)	$HCCl_3$	3489	3471	3460	3457	3467
	CCl_4	3483	3470	3460	3455	3460
	CS_2	3475	3466	3452	3453	3456
DE (diethyl)	$HCCl_3$	———	3471	3459	3458	3466
	CCl_4		3474	3459	3460	3461
	CS_2		3466	3453	3454	3457
DP (di-n-propyl)	$HCCl_3$	3489	———	3458	3459	3466
	CCl_4	3484		3460	3460	3461
	CS_2	3476		3454	3456	3457
DiP (di-i-propyl)	$HCCl_3$	3505 3491	3493 sh	3483 3464	3481 3462	3482 sh
	CCl_4	3498 3479	3490 sh	3479 3458	3480 3460	3482 3455
	CS_2	3494 3472	3484 3464	3478 3452	3477 3454	3480 3452
DB (di-n-butyl)	$HCCl_3$	———	———	———	3458	3466
	CCl_4				3459	3462
	CS_2				3455	3459
DiB (di-i-butyl)	$HCCl_3$	3489	———	3459	3466	3468
	CCl_4	3483		3460	3462	3462
	CS_2	3476		3459	3458	3461
DcH (di-cyclohexyl)	$HCCl_3$	3505 3489	3490 sh	3481 sh	3479 sh	3485 3463
	CCl_4	3495 3481	3487 sh	3478 3460	3477 sh	3478 3455
	CS_2	3492 3472	3482 3464	3477 3454	3474 3454	3478 3451
cHM (cyclohexyl, methyl,)	$HCCl_3$	3486	———	3461	———	3461
	CCl_4	3484		3461		3462
	CS_2	3474		3452		3457

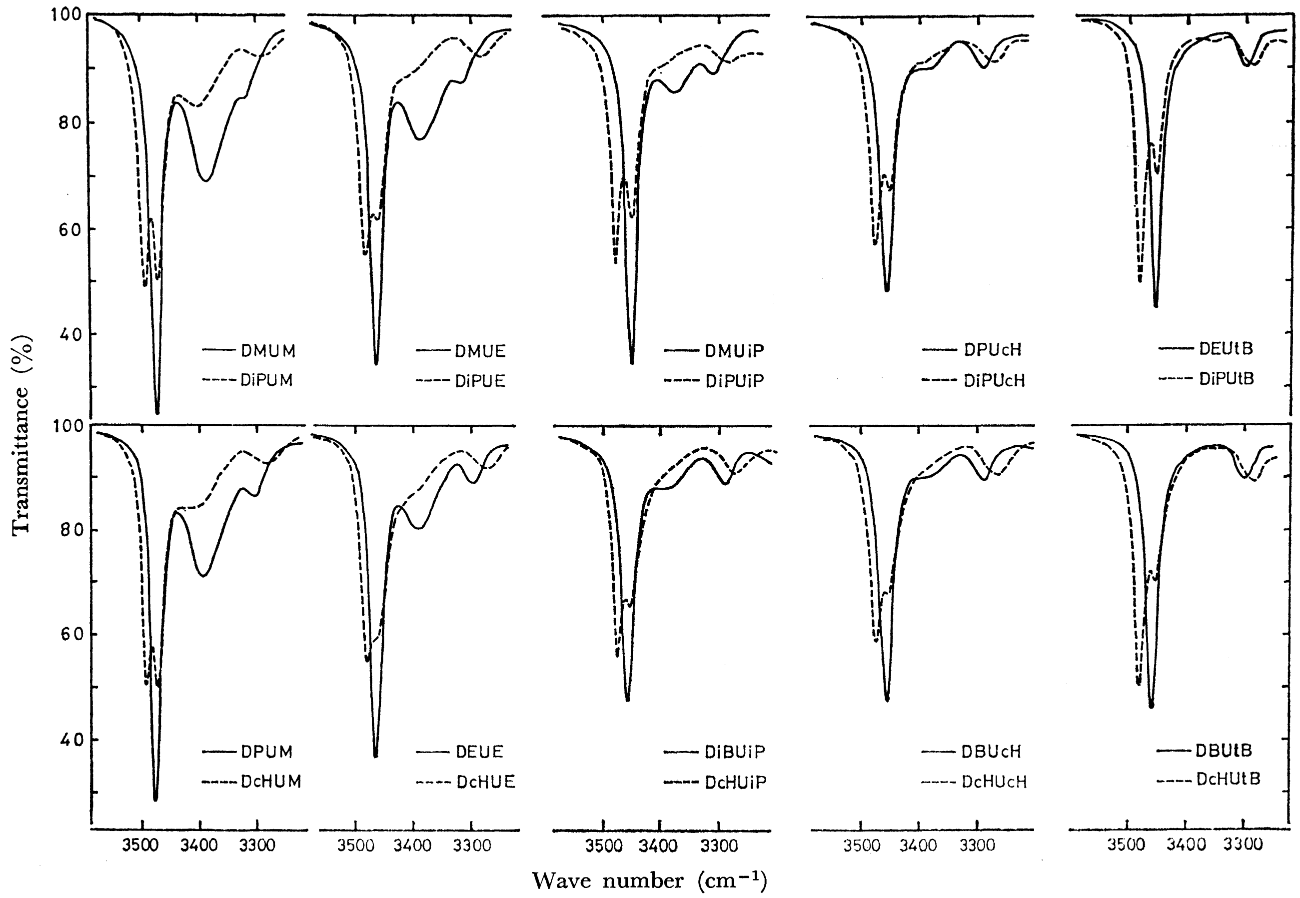
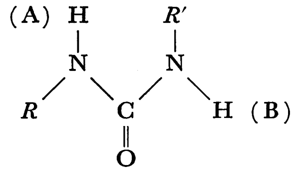


Fig. 1. The free N-H stretching absorption bands of various R_2UR' in CS_2 (0.02 M).

of the *R'* group. Even cHMU*t*B, with the $C_6H_{11}\text{–}\overset{CH_3}{\overset{|}{N}}\text{–}$ group of a sterically medium size, exhibited only one N–H band.

Examining the band intensities of R_2U*R'* in Fig. 1, one can understand easily that the higher N–H band appears at the expense of the intensity of the *trans* N–H band (the lower band). Therefore, the higher band may be concluded to originate from a certain rotational isomer which is mainly caused by the steric hindrance of the *R* groups and the C=O group, and that this band corresponds to the very weak band at 3469 cm^{-1} of *s*-D*t*BU in CCl_4.

On the assumption that the 3469 cm^{-1} band of *s*-D*t*BU arises from the *cis* form in the *trans-cis* configuration, consider the substitution of another bulky group for either of the two imino hydrogen atoms on *R*U*R'* with the *trans-cis* configuration.



trans-cis

If the hydrogen atom at the A site is substituted for a bulky group, the steric hindrance between the substituent and the *R'* group may be more serious than that between the C=O and the *R'* groups in the case of the *trans* form. Accordingly, this substitution will favor the *trans* configuration. On the other hand, another substitution at the B site leaves the *trans* configuration. Thus, if the weak 3469 cm^{-1} band of *s*-D*t*BU arises from the *cis* form, the corresponding band of trialkylureas with bulky groups may be expected to be weak or absent.

Let us consider *N*-cyclohexyl-*N'*-*t*-butylurea (cHU*t*B) and *N*-dicyclohexyl-*N'*-*t*-butylurea (DcHU*t*B) as examples. We have previously reported that the spectrum of cHU*t*B in $CHCl_3$ shows a weak band at 3471 cm^{-1} corresponding to the 3469 cm^{-1} band of *s*-D*t*BU.[4] In the spectrum of DcHU*t*B in Fig. 1, the corresponding band appears strongly at 3478 cm^{-1} and is even stronger than the *trans* N–H band at 3451 cm^{-1}, contrary to the expectation based on the above assumption. These observations clearly indicate that the coexisting rotational isomer of *s*-D*t*BU in solution is not in the *trans-trans* configuration.

All the spectra of D*i*PU*R'* and DcHU*R'* examined in this study have a band corresponding to the 3478 cm^{-1} band of DcHU*t*B. As has been mentioned above, this band appears when two *R* groups on R_2U*R'* are isopropyl or cyclohexyl groups, either of which is bulkier than the other groups. Unfortunately, no R_2U*R'* with the bulkiest *R* group, *t*-butyl, could be examined.

It is quite evident from Fig. 1 that the bulkier the effective size of the *R'* group on R_2U*R'*-II is, the stronger the intensity of this band becomes at the expense of that of the *trans* N–H band. This indicates that probably the steric hindrance between the *R'* and the

TABLE 2. THE C=O (AMIDE I) STRETCHING FREQUENCIES OF R_2NCONH*R'* (0.02 mol/l IN CCl_4)

R$_2$	*R'*: M	E	*i*P	cH	*t*B
DM	1668	1667	1665	1667	1672
DE	———	1660	1658 1651	1659 1651	1665
DP	1663	———	1659 1652	1659 1652	1665
D*i*P	1659 1640	1659 1651	1658 1652 1638	1658 1652 1645	1659 1654
DB	———	———	———	1658 1651	1663
D*i*B	1663	———	1658 1651	1659 1652	1664
DcH	1658 1652 1649	1658 1652 1644	1658 1651 1645	1658 1651 1640	1658 1653
cHM	1660 1654	———	1659 1654	———	1661

TABLE 3. THE C=O (AMIDE I) AND C-N (AMIDE II) STRETCHING FREQUENCIES OF R_2NCONH*R'* (0.02 mol/l in $CHCl_3$)

R$_2$	*R'*: M		E		*i*P		cH		*t*B	
	I[a]	II[a]	I	II	I	II	I	II	I	II
DM	1642	1533	1640	1524	1640	1520	1633	1513	1641	1520
DE	———	———	1633	1518	1630	1510	1632	1510	1634	1513
DP	1638	1525	———	———	1630	1510	1630	1509	1633	1514
D*i*P	1623	1516	1624	1513	1620	1510 1502	1621	1512 1505	1623	1511
DB	———	———	———	———	———	———	1628	1508	1633	1513
D*i*B	1639	1525	———	———	1628	1509	1629	1512	1635	1512
DcH	1622	1515	1620	1514	1619	1510 1505	1620	1512 1505	1642 1625	1512
cHM	1632	1520	———	———	1625	1510	———	———	1634	1512

a) I : C=O stretch (Amide I), II : C-N stretch (Amide II).

C=O groups plays an important role in determining the amount of the coexisting rotational isomer.

As for the associated N–H band of all the R_2UR' substances on the lower-frequency side of the *trans* N–H band, it may be seen that the bulkier the effective size of substituents is, the weaker the intensity of this band becomes.

From the above discussion, it may be concluded that the serious steric hindrance prevents the two *R* groups from leaving the skeletal plane, and that, at the same time, this effect makes the N–H bond out-of-plane, but cannot convert the N–H bond into the *cis* position. That is, the 3469 cm^{-1} band of *s*-D*t*BU arises from a form in which the N–H group is out-of-plane owing to the steric hindrance (we will call this form the *out* form hereinafter), and the rotational isomers with the *trans-trans* (dominant) and probably *out-out* configurations may coexist in solutions of *s*-D*t*BU.

In the case of R_2UR'-II, it may be seen that the amount of the coexisting *out* configuration increases with the bulkiness of the effective size of the R' group; R_2UM-II=50%, R_2UE-II=55%, R_2U*i*P-II≈R_2UcH-II=60%, and R_2U*t*B-II=65%.

The C=O and C–N Stretching Band. The C=O stretching frequencies of R_2UR' in CCl_4 and $CHCl_3$ are shown in Tables 2 and 3 respectively. The frequencies of R_2UR' in CCl_4 are higher by 24—38 cm^{-1} than those in $CHCl_3$; this indicates that the hydrogen bonding between the proton of $CHCl_3$ and the C=O group is formed in the $CHCl_3$ solution.

The C=O stretching frequencies of R_2UR' in the same solvent are similar, though those of DMUR' are somewhat higher in either solvent. However, it should be noted that the main C=O stretching band of R_2UR'-II appears at a frequency lower than that of R_2UR'-I by ~10 cm^{-1} and has a few prominences, as is shown in Fig. 2.

The C–N stretching bands of some R_2UR'-II substances in $CHCl_3$ appear at a frequency lower than those of R_2UR'-I, and others have an additional band (Table 3).

This work was supported by a grant from the Ministry of Education.

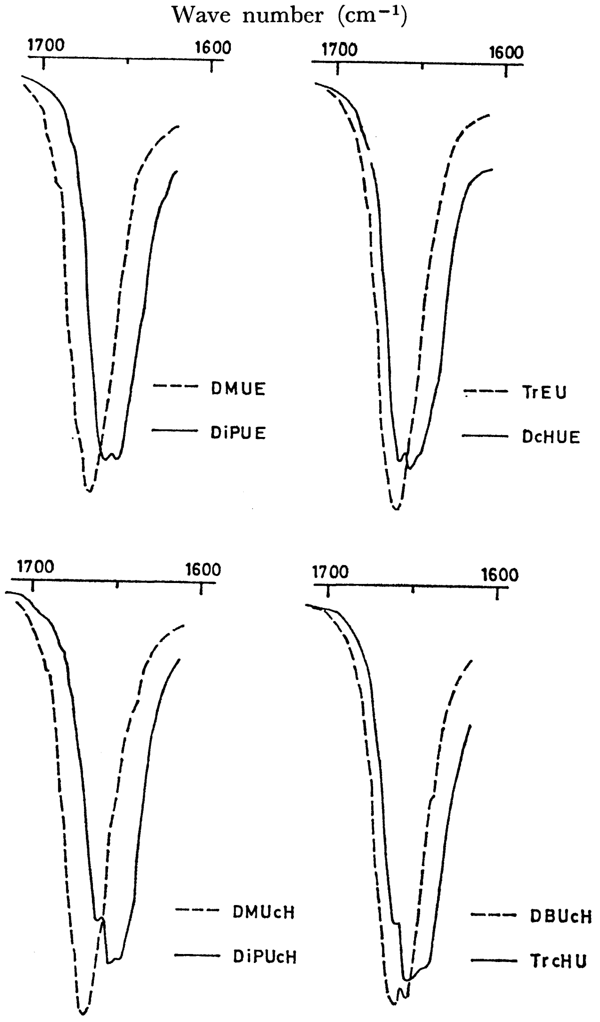


Fig. 2. The C=O stretching absorption bands of some R_2UR' in CCl_4 (0.02 M).

References

1) Y. Mido, *Spectrochim. Acta*, **29A**, 1 (1973).
2) Y. Mido, *ibid.*, **29A**, 431 (1973).
3) Y. Mido, This Bulletin, **47**, 1833 (1974).
4) Y. Mido, *Spectrochim. Acta*, to be published.
5) C. N. R. Rao, G. C. Chaturvedi, and R. K. Gosavi, *J. Mol. Spectrosc.*, **28**, 526 (1968).