Stereodynamics at Two Nitrogen Atoms in Bicyclic Biurethanes. A Possible Concomitant Double Inversion and Double Rotation

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Summary Variable temperature ^{13}C n.m.r. spectra of bicyclic biurethanes have revealed that double inversion at the two nitrogen centres takes place as well as double rotation about two >N–CO bonds.

VARIABLE temperature ^{1}H[1] and ^{13}C[2] n.m.r. studies have revealed a *trans* ⇌ *trans* double inversion at the two nitrogen atoms of bicyclic hydrazines (**1**) and (**2**), and it is interesting to see whether this inversion also occurs in bicyclic biurethanes such as (**3**)—(**8**). Using ^{1}H n.m.r., Anderson and Lehn[3] observed two rate processes (at high and low temperatures) for (**4**) and only one rate process (at low temperature) for (**3**). Based on the assumption that the amide nitrogen atom is planar, they suggested that the low-temperature process common to (**3**) and (**4**) is the hindered >N–CO bond rotation while the high-temperature process is due to 'bridge-flipping,' which is possible only for the conformationally more flexible system of (**4**). We have now examined the variable temperature ^{13}C n.m.r. spectra of compounds (**5**)—(**8**).† The results are summarised in the Table.

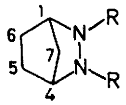
TABLE Chemical shifts of compounds (**5**)—(**8**)[a]

	Temp /°C	C(1), C(4)	C(5), C(6)	C(7)	C=O	-OCH$_2$-	Me
(**5**)	76·0	60·7	27·6	37·6	158·6	62·0	14·5
	−16·3	60·8	28·6	37·4	161·1	62·1	13·8
		60·3	27·5		160·4	61·6	
		59·8	26·3		160·1		
					159·4		
(**6**)	84·4	65·5	137·7	47·9	160·0	61·9	14·0
	7·8	65·3	139·2	47·6	158·9	61·9	13·5
			134·5				
	−24·7	65·0	140·0	47·5	158·7	61·8	13·8
			138·4				
			134·3				

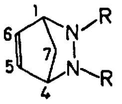
	Temp /°C	C(1), C(4)	C(5), C(6)	C(7), C(8)	C=O	-OCH$_2$-	Me
(**7**)	142·2	48·9	23·4		157·3	61·5	14·2
	50·1	48·9	25·1	22·0	157·8	61·7	14·6
	−5·0	49·0	24·2	21·8	157·4	61·6	13·9
		48·2		20·6	157·1		
					156·9		
(**8**)	139·7	50·3	134·4	21·8	158·5	61·7	13·9
	29·5	50·3	135·3	23·0	159·7	62·1	13·8
			132·3	19·7	158·2		
	−27·3	49·9	136·1	23·0	157·5	61·2	13·2
			134·7	21·9			
			132·3	18·9			

[a] Chemical shifts from internal standards were converted to δ (Me_4Si).

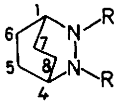
Contrary to the finding of Anderson and Lehn,[3] compound (**6**) as well as (**7**) and (**8**) exhibited two rate processes. At higher temperature, C(5) and C(6) of (**6**) gave one sharp singlet, which split into two peaks of nearly equal intensity at 7·8 °C. On further cooling, the lower of the two peaks split again into two further peaks. The C(5) and C(6), and C(7) and C(8) signals of (**8**) showed similar splittings for the two rate processes, while for C(5), C(6), C(7) and C(8) of (**7**), the higher of the two peaks split in the low-temperature process. Though (**5**) exhibited only one rate process (only one T_c), the splitting is of the type described above, indicating that two processes took place at essentially the same temperature.



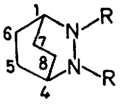
(1); R = Me
(5); R = CO_2Et



(2); R = Me
(3), R = CO_2Me
(6), R = CO_2Et



(7) R = CO_2Et



(4) R = CO_2Me
(8) R = CO_2Et

Evidently the low-temperature process is due to the hindered >N–CO rotation. Thus, the C(1) and C(4) signal of (**7**), which should be a singlet as long as the >N–CO rotation is rapid, splits into two peaks at lower temperature. The high-temperature process may be brought about by the torsion about the N–N bond (with two planar nitrogen atoms) and/or the out-of-plane distortion at the two nitrogen atoms (*i.e.*, essentially double inversion). The non-equivalence of C(5) and C(6) of (**6**) as well as C(5) and C(7), C(6) and C(8) of (**7**) affected by the high-temperature process strongly favours the latter interpretation. The chemical shift differences 4·7 p.p.m. for (**6**) and 3·1 p.p.m. for (**7**) are compatible with the difference of C(6) shifts between methyl *exo*- and *endo*-norbornane-2-carboxylate (3·6 p.p.m.; due to γ-effect).[4] The fact that only one of the two peaks splits at low-temperature may be rationalised by assuming that only the bridge carbon(s) closer to the N–CO_2Et group are susceptible to the slow rotation of the >N–CO bond.

Full line-shape analyses and estimated activation parameters will be reported in the full paper.

(*Received*, 2*nd December* 1974; *Com.* 1454.)

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† ^{13}C n.m.r. spectra were determined using a JEOL 60-HL (CW mode) spectrometer.

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