



Fig. 1. Effect of the addition of the free radical TEMPO on the linewidth of NH resonances in I: Ala (○), Me (▲), Cys(1) (●), and Cys(3) (△).

on going from an apolar, poorly hydrogen-bonding solvent like CDCl_3 to a polar, strongly hydrogen-bonding solvent like $(\text{CD}_3)_2\text{SO}$. The other three NH groups move to substantially lower field in $(\text{CD}_3)_2\text{SO}$, as compared with CDCl_3 . In CDCl_3 , the $d\delta/dT$ value observed for Ala NH and NHMe are markedly larger than for the Cys(1) and Cys(3) NH groups. Large $d\delta/dT$ values in an apolar solvent like CDCl_3 could arise from breakage of *intermolecular* hydrogen bonding between peptide molecules.^{8,9} A study of concentration dependence of NH chemical shifts in CDCl_3 over the range 2–25 mM suggests that intermolecular effects are significant only for the Ala NH group and, to a lesser extent, for the terminal NHMe group.

The nmr data provide strong support for the solvent-shielded nature of Cys(1) and Cys(3) NH groups in CDCl_3 . This is fully consistent with their involvement in intramolecular hydrogen bonding, as shown in Fig. 2. In polar solvents like

TABLE I
¹H-NMR Parameters^a for Peptide NH Groups in Boc-L-Cys-L-Ala-L-Cys-NHMe (I)

	δ (ppm)		$d\delta/dT$	
	CDCl_3	$(\text{CD}_3)_2\text{SO}$	CDCl_3	$(\text{CD}_3)_2\text{SO}$
Cys(1)	5.47	6.98	0.0042	0.0095
Ala(2)	6.66	8.85	0.0147	0.0034
Cys(3)	7.69	7.45	0.0042	0.0014
NHMe	7.09	7.98	0.0086	0.0041

^a Chemical-shift (δ) values are with respect to internal Me_4Si .

^b $d\delta/dT$ values are expressed as ppm/K.

