Hydrogen Bonding in a 'Folded' Dimer: the Crystal Structure of *N*-Hydroxy-5,5-dimethyl-2-pyrrolidone

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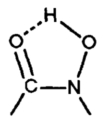
In the crystalline state the title compound forms hydrogen-bonded pairs in which the planes of the two amide units are almost orthogonal.

A recent discussion of multiple hydrogen bonding between pairs of molecules cites 22 'representative examples' from the recent literature.[1] Except where these examples involve flexible or puckered components such as crown ethers, the interacting partners occupy a common plane, as encountered in carboxylic acids or nucleotide base pairs. It occurred to us that 'folded' pairing might be possible for any hydroxamic acids which adopt an s-*cis* conformation of the amide unit (*i.e.* with the two oxygens on the same side of the C–N bond). Inspection of models indicated that almost perfect alignment of two O–H···O hydrogen bonds should be possible in a dimer structure whose 'fold' passes through the two hydroxy oxygen atoms (Fig. 1). This type of association, which recognises the electronic preference for out-of-plane OH groups in hydroxamic acids,[2] could accommodate the strong hydrogen bonding apparent in solution spectra of these molecules,[2] an observation which is commonly attributed to in-plane intramolecular H-bonds, structure **1**.[2,3] AM1 calculations on simple models were in accord with this type of dimeric structure being significantly more stable than the most favourable monomer conformation.

Previously reported crystal structures of *N*-alkylated hydroxamic acids[4] corroborate the out-of-plane nature of the hydroxy group, but in most cases the amide unit is s-*trans*, and hydrogen bonding results in infinite molecular chains, structure **2**. Some primary hydroxamic acids do adopt the s-*cis* conformation but the structures of these are complicated by additional hydrogen bonding. This frequently arises not only because of the NH group, but also from the presence of other features, for example the presence of water molecules in crystalline acetohydroxamic acid.[5] Whilst association of the kind illustrated in Fig. 1 *can* be discerned in one literature example, namely salicylohydroxamic acid,[6] this feature was not highlighted in the original paper, which instead emphasised the three-dimensional network of hydrogen bonds involving additionally both the phenolic and the NH groups.

We considered that this type of association was deserving of further attention, since it should afford a supramolecular feature capable of bringing substituent groups on separate molecules into close proximity.



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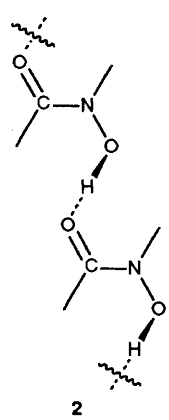

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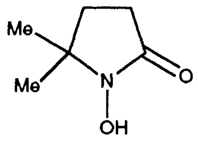

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In order to investigate the possibility of dimer formation in the absence of additional hydrogen-bonding effects, we have therefore examined the cyclic *N*-alkylhydroxamic acid **3**,[7] in which s-*cis* amide geometry is imposed by the pyrrolidone ring. The results of an X-ray structure analysis on **3**, displayed in Fig. 2, bear out the generalisation depicted in Fig. 1.‡ There is a slight deviation from perfect C_2 symmetry in the pair, presumably resulting from crystal packing factors. The hydrogen bonds, at 2.61 and 2.66 Å, are quite strong (the H···O distances are 1.61 and 1.70 Å), and are both almost linear (OHO angles 180 and 172°). The hydroxy groups are twisted 77 and 74° out of plane, and the fold angle, α (Fig. 2), between the two amide planes, is *ca.* 101°.

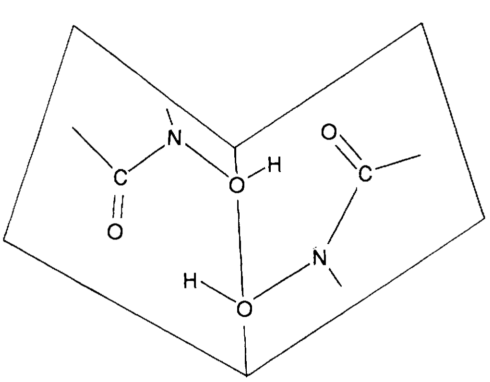

Fig. 1 'Folded' dimer model

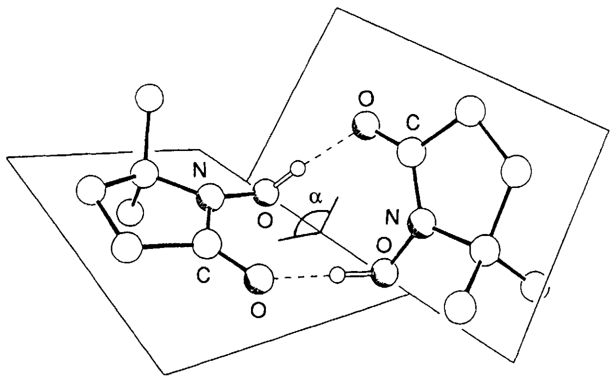

Fig. 2 Crystal structure of the hydroxamic acid **3**

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‡ *Crystal data* for **3**: $C_6H_{11}NO_2$, M = 129.2, monoclinic, a = 10.708(2), b = 10.859(2), c = 12.698(2) Å, β = 102.52(2)°, U = 1441 Å^3, space group $P2_1/n$, $Z = 8$ (2 crystallgoraphically independent molecules), D_c = 1.19 g cm^{23}, μ = 7.4 cm^{21}. Data were measured on a Siemens P3/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The hydrogen atoms involved in hydrogen bonding were refined isotropically; the remainder were constrained with fixed isotropic thermal parameters. R = 0.049, R_w = 0.054 for 1557 independent observed reflections [$|F_o| > 4\mu(|F_o|)$, $2\theta \leq 116°$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We are currently examining the strength of this type of association and its variation with the size of the lactam ring. A preliminary osmometric study of **3** in toluene has given a solution relative molecular mass of *ca.* 230 (M_r of **3** = 129), confirming that dimeric association is substantially retained in a non-polar solvent. In carbon tetrachloride, the IR spectrum of **3**, which shows a broad OH band between *ca.* 3450 and 2500 cm^{-1} and a sharp carbonyl at 1687 cm^{-1}, remains essentially unchanged between *ca.* 1.5 and 0.015 mol dm^{-3}.

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References

1 T. J. Murray and S. C. Zimmerman, *J. Am. Chem. Soc.*, 1992, **14**, 4010.
2 L. Bauer and O. Exner, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 376.
3 F. G. Bordwell, H. E. Fried, D. L. Hughes, T.-Y. Lynch, A. V. Satish and Y. E. Whang, *J. Org. Chem.*, 1990, **55**, 3330.
4 *E.g.* W. L. Smith and K. N. Raymond, *J. Am. Chem. Soc.*, 1980, **102**, 1252; A. Dietrich, D. R. Powell, D. L. Eng-Wilmot, M. B. Husain and D. van der Helm, *Acta Crystallogr., Sect. C*, 1990, **46**, 816 and references therein.
5 B. H. Bracher and R. W. H. Small, *Acta Crystallogr., Sect. C*, 1970, **26**, 1705.
6 I. K. Larsen, *Acta Crystallogr., Sect. B*, 1978, **34**, 962.
7 R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland and A. Todd, *J. Chem. Soc.*, 1959, 2094.