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A 1:1 molecular complex of 4-methylpyridine *N*-oxide and saccharin

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The crystal structure of the 1:1 molecular complex of 4-methylpyridine *N*-oxide and saccharin, $C_6H_7NO{\cdot}C_7H_5NO_3S$, is built up of heterodimers of the constituent molecules. This structure is stabilized by an eight-membered supramolecular synthon consisting of N—H···O(−) and C—H···O hydrogen bonds.

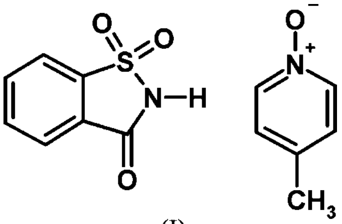
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.047
wR factor = 0.119
Data-to-parameter ratio = 12.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Saccharin is a moderately strong acid, and crystals of the title complex, (I), were obtained during the course of our recent work on the use of saccharin in pharmaceutical chemistry (Banerjee *et al.*, 2005). X-ray quality single crystals of (I) were obtained when a 1:1 molar ratio of saccharin and 4-methylpyridine *N*-oxide were cocrystallized from methanol. Complex (I) illustrates a situation wherein a crystal structure is stabilized by strong and weak intermolecular interactions (Desiraju, 2005). The molecular geometry and atom numbering of (I) are given in Fig. 1. In the crystal structure of (I) (space group $P2_1/c$) the saccharin NH group hydrogen bonds to 4-methylpyridine *N*-oxide *via* N—H···O(−) and C—H···O hydrogen bonds to form an eight-membered amide–*N*-oxide-type supramolecular synthon. This synthon has been observed only recently by Reddy *et al.* (2006) during the course of their work on the use of the pyridine *N*-oxide functionality to prepare novel pharmaceutical cocrystals. Fig. 2 shows a packing diagram of (I) viewed down the [001] axis. The geometry of the intermolecular interactions is given in Table 1. In the crystal structure, the 4-methylpyridine *N*-oxide–saccharin heterodimer units are connected to each other *via* C—H···O═S hydrogen bonds. This forms a zigzag network that propagates along the *b* axis. This two-point amide–*N*-oxide-type synthon is worth 12.41 kcal mol^{-1} [631–G(*d*,*p*)/B3LYP (*GAUSSIAN03*; Frisch *et al.*, 2003)], which is comparable to the value reported by Reddy *et al.* (2006) (11–12 kcal mol^{-1}). It is also interesting to note that this is the first report of a pyridine *N*-oxide–*o*-sulfobenzimide synthon.



(I)

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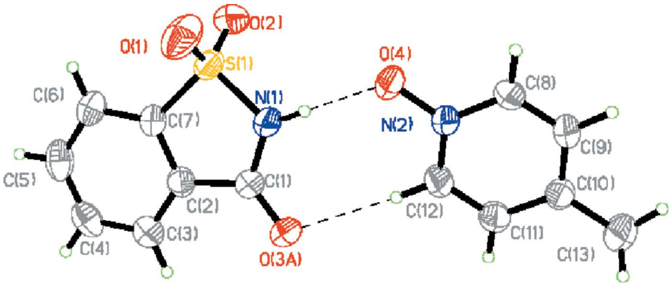

Figure 1
View of the title molecular complex, with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

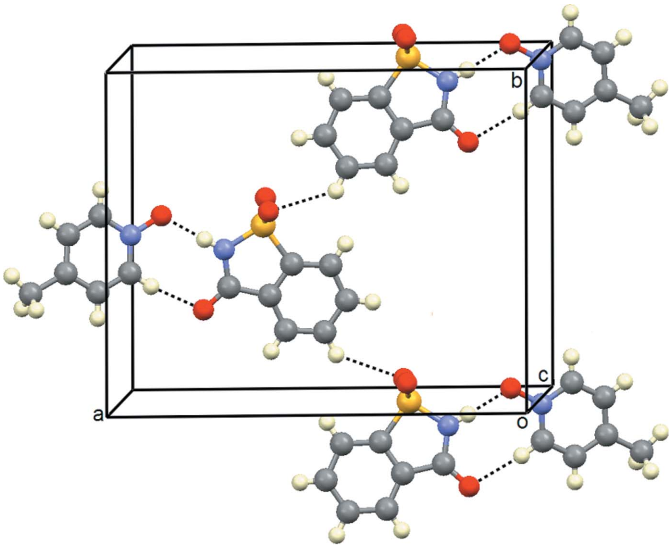

Figure 2
Packing diagram of (I). Note the eight-membered supramolecular synthons and connecting C—H···O hydrogen bonds (dashed lines).

Experimental

Saccharin (40 mg, 0.2 mmol) was dissolved in methanol (10ml) and 4-methylpyridine *N*-oxide (20 mg, 0.2 mmol) was added. The solution was warmed in a water bath for five minutes and filtered. The filtrate was allowed to cool to room temperature. X-ray quality single crystals were obtained after two days. Interestingly, when bulk crystallization was attempted (more than 500 mg of the component) the quality of the crystals obtained was considerably poorer.

Crystal data

$C_6H_7NO{\cdot}C_7H_5NO_3S$
$M_r = 292.31$
Monoclinic, $P2_1/c$
$a = 14.960\ (3)$ Å
$b = 12.330\ (3)$ Å
$c = 7.3565\ (15)$ Å
$\beta = 100.24\ (3)^\circ$
$V = 1335.3\ (5)$ Å^3
$Z = 4$
$D_x = 1.454$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.26$ mm^{-1}
$T = 298\ (2)$ K
Block, colorless
0.14 × 0.12 × 0.11 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{\min} = 0.962$, $T_{\max} = 0.970$
4457 measured reflections
2345 independent reflections
1569 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.119$
$S = 1.01$
2345 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.4791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O2$^{\rm i}$	0.93	2.57	3.267 (4)	132
N1—H1···O4	0.83 (3)	1.78 (3)	2.605 (3)	175 (4)
C12—H12···O3	0.93	2.32	3.229 (4)	166

Symmetry code: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

C-bound H atoms were treated as riding, with C—H distances of 0.93 (aromatic) and 0.96 Å (methyl), and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C_{aromatic}})$ or $1.5U_{\rm eq}({\rm C_{methyl}})$. The N-bound H atom was refined freely.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT* and *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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