The Crystal Structure of a Hydrogen-Bonded 1:2 Adduct between N,N,N',N'-Tetramethylglutaramide and Trifluoromethanesulfonic Acid. An Example of Double Proton Transfer

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The crystal structure of the title compound, $(CH_3)_2NCO(CH_2)_3CON(CH_3)_2 \cdot 2CF_3SO_3H$, has been determined at $-135\,°C$ from X-ray diffraction data. Full-matrix, least-squares refinement based on 3482 observed reflections gave a final conventional R of 0.044. The crystals are monoclinic: $a = 11.183(3)$, $b = 14.626$ (3), $c = 13.401(3)$ Å; $\beta = 114.80(2)°$; $Z = 4$; space group $P2_1/c$. In the adduct, both amide carbonyl groups are protonated and strongly hydrogen-bonded to a trifluoromethanesulfonate anion. Some average bond lengths and angles are: $C-O(H) = 1.307$, $O-H = 0.81$, $O\cdots O = 2.574$ and $N-C(O) = 1.297$ Å; $\angle O-H\cdots O = 166$ and $\angle C-O-H = 112°$.

During our work on intramolecular cyclization reactions of diamides with trifluoromethanesulfonic anhydride,[1] the reaction involving N,N,N',N'-tetramethylglutaramide in the presence of traces of water gave an unexpected product. This compound had IR absorption bands in the range of 2500–2700 cm^{-1}, indicating relatively strong hydrogen bonding.[2] As part of an ongoing investigation of hydrogen-bonded complexes,[3] an investigation of the structure of this reaction product is now reported.

Experimental

Synthesis. The procedure is described in Ref. 1 and is the one designed to give a cyclic dication ether. Upon recrystallization from acetonitrile, colourless crystals, m.p. 153–155 °C (slight decompn.), were formed.

X-ray data. An Enraf-Nonius CAD-4 diffractometer with graphite-monochromated MoKα ra-diation was used for the determination of the unit cell dimensions ($\lambda\alpha_1 = 0.70926$, $\lambda\alpha_2 = 0.710354$ Å) and the recording of intensity data ($\lambda\alpha = 0.71069$ Å). During measurements, the crystal site was kept at $-135\,°C$. The crystal size was $\sim 0.5 \times 0.1 \times 0.15$ mm. Cell parameters were determined from a least-squares fit to the diffractometer settings of 25 general reflections. The crystals are monoclinic, space group $P2_1/c$ (No. 14) with $a = 11.183(3)$, $b = 14.626(3)$, $c = 13.401(3)$ Å, $\beta = 114.80(2)°$, $Z = 4$, $d_x = 1.620$, μ (MoKα) = 3.49 cm^{-1}. The intensity data were recorded using the ω scan technique with a constant scan rate of 4° min^{-1} and a minimum scan width of 1.80°, including background scans of 0.30° at the beginning and at the end of each scan. Crystal orientation was checked at intervals of 200 recordings, and 3 standard reflections were remeasured every 2 h. All 4801 unique reflections with 2θ ≤ 56° were measured. Of these, 3482 were observed while the remainder had $I \le 2\sigma(I)$ and were regarded as unobserved. The computer programs used in this investigation were supplied by Enraf-Nonius (SDP-plus 1983 and CAD 4-OS11).

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Table 1. Positional parameters and their estimated standard deviations.[a]

Atom	x	y	z	$B(Å^2)$
S1	0.42193(6)	0.40262(4)	0.25626(5)	2.28(1)
O11	0.4483(2)	0.4676(2)	0.1859(1)	3.84(5)
O12	0.4461(2)	0.3098(1)	0.2396(2)	4.53(5)
O13	0.4686(2)	0.4320(1)	0.3675(1)	3.03(4)
C10	0.2444(2)	0.4108(2)	0.2045(2)	3.04(6)
F11	0.2077(2)	0.4947(1)	0.2127(2)	6.45(6)
F12	0.1982(1)	0.3576(1)	0.2602(1)	4.44(4)
F13	0.1849(2)	0.3855(2)	0.1008(1)	5.86(5)
S2	1.05560(5)	0.69522(4)	0.63295(5)	2.12(1)
O21	0.9562(2)	0.7614(1)	0.6272(1)	2.74(4)
O22	1.0030(2)	0.6143(1)	0.5694(1)	2.45(4)
O23	1.1573(2)	0.6813(1)	0.7404(1)	3.38(4)
C20	1.1380(3)	0.7526(2)	0.5588(2)	3.07(6)
F21	1.0555(2)	0.7712(1)	0.4564(1)	4.35(4)
F22	1.2324(2)	0.6991(1)	0.5546(1)	5.23(4)
F23	1.1928(2)	0.8306(1)	0.6062(1)	4.58(4)
C1	0.4524(2)	0.8120(2)	0.4862(2)	2.66(5)
C2	0.3964(2)	0.6614(2)	0.3908(2)	2.71(6)
N1	0.4979(2)	0.7262(1)	0.4572(1)	2.00(4)
C3	0.6226(2)	0.7095(2)	0.4919(2)	1.99(5)
O1	0.7027(2)	0.7742(1)	0.5492(1)	2.44(4)
C4	0.6763(2)	0.6222(2)	0.4699(2)	2.01(5)
C5	0.6938(2)	0.6238(2)	0.3622(2)	2.08(5)
C6	0.7553(2)	0.5329(2)	0.3514(2)	1.98(5)
C7	0.7619(2)	0.5236(2)	0.2428(2)	2.02(5)
O2	0.6568(2)	0.4994(1)	0.1566(1)	2.43(4)
N2	0.8663(2)	0.5400(1)	0.2263(1)	2.01(4)
C8	0.9910(2)	0.5727(2)	0.3115(2)	2.68(5)
C9	0.8667(2)	0.5202(2)	0.1190(2)	2.65(5)
HO1*	0.785(3)	0.760(2)	0.571(2)	6.2(9)
HO2*	0.602(3)	0.485(2)	0.172(2)	4.1(7)

[a]Starred atoms (*) were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

Structure determination

The intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved using direct methods (MULTAN), and refined in the same manner as described in Ref. 3 with $w = (\sigma(F)^2 + (0.03F)^2 + 5.0)^{-1}$. In the least-squares refinement, non-hydrogen atoms were given anisotropic temperature coefficients, while hydrogen atoms were refined isotropically. The refinement converged, giving a conventional $R = 0.044$, $R_w = 0.045$, $S = 1.49$. A final difference map showed a maximum electron density of 0.3 $e^-/Å^3$.

Results and discussion

Atomic parameters are listed in Table 1, interatomic distances and angles in Tables 2 and 3, and molecular planes and interplanar angles in Table 4. Tables of observed and calculated structure factors, anisotropic temperature factors and aliphatic hydrogen atom parameters are available from one of the authors (K.M.-M.). Fig. 1 shows the structure of the hydrogen-bonded complex with labelling of atoms.

During the refinement of the structure it soon became clear that both amide groups in the N,N,N',N'-tetramethylglutaramide molecule

were protonated. Both protons had been transferred to the carbonyl oxygens of the amide groups. They probably originally belonged to trifluoromethanesulfonic acid molecules which had been generated from the anhydride in the presence of moisture during preparation. Characteristically, each protonated carbonyl group is strongly hydrogen-bonded to a trifluoromethanesulfonate anion (Fig. 1). There are no other short intra- or intermolecular contacts. Bond lengths and angles in the carbon chain in the amide are normal.

The amide groups. Both amide groups are approximately planar. These planes make an angle of 62.5°, being nearly at right angles to the central C4, C5, C6 plane (Table 4). The protonated C−OH groups are on either side of this central plane.

The angle sums on the nitrogen and carbonyl carbon atoms are all about 360°, corresponding to sp^2 hybridization of these atoms. Average bond lengths in the amide groups are: C−N = 1.465, N−C(O) = 1.297 and C−O(H) = 1.307 Å. Typical bond lengths for N−C(O) and C=O in amides are 1.33 and 1.23 Å.[4]

In Table 5, some bond lengths and angles in a selection of amides are shown. Both unprotonated amides *(1–4)*,[5,7–9] "partially protonated" amides *(5–7)*,[10–12] and fully protonated amides *(8–11,* where *11* has formally added $C_2H_5^+$ in-

Table 3. Interatomic angles (°) with e.s.d. in parentheses.

C1−N1−C2	116.7(2)	S1−C10−F13	111.9(2)
C1−N1−C3	120.6(2)	F11−C10−F12	107.0(2)
C2−N1−C3	122.7(2)	F11−C10−F13	108.3(2)
N1−C3−O1	116.3(2)	F12−C10−F13	106.6(2)
N1−C3−C4	123.6(2)	C10−S1−O11	101.3(1)
O1−C3−C4	120.1(2)	C10−S1−O12	104.7(1)
C3−C4−C5	113.1(2)	C10−S1−O13	104.1(1)
C4−C5−C6	108.4(2)	O11−S1−O12	114.8(1)
C5−C6−C7	112.3(2)	O11−S1−O13	113.4(1)
C6−C7−O2	119.6(2)	O12−S1−O13	116.3(1)
C6−C7−N2	124.3(2)	S2−C20−F21	111.7(2)
O2−C7−N2	116.1(2)	S2−C20−F22	110.1(2)
C7−N2−C8	124.0(2)	S2−C20−F23	112.0(2)
C7−N2−C9	120.1(2)	F21−C20−F22	107.3(2)
C8−N2−C9	115.8(2)	F21−C20−F23	107.6(2)
C3−O1−HO1	113(2)	F22−C20−F23	108.1(2)
C7−O2−HO2	111(2)	C20−S2−O21	102.4(1)
O1−HO1···O21	165(3)	C20−S2−O22	103.4(1)
O2−HO2···O11	167(3)	C20−S2−O23	104.2(1)
HO1···O21−S2	134(1)	O21−S2−O22	113.9(1)
HO2···O11−S1	128(1)	O21−S2−O23	114.7(1)
S1−C10−F11	111.2(2)	O22−S2−O23	115.9(1)
S1−C10−F12	111.6(2)		

Table 2. Interatomic distances (Å) with e.s.d. in parentheses.

C1−N1	1.466(3)	S1−O11	1.454(2)
C2−N1	1.460(3)	S1−O12	1.420(2)
N1−C3	1.295(3)	S1−O13	1.424(1)
C3−O1	1.308(2)	C20−F21	1.321(3)
C3−C4	1.492(3)	C20−F22	1.334(3)
C4−C5	1.537(3)	C20−F23	1.324(3)
C5−C6	1.531(3)	C20−S2	1.819(2)
C6−C7	1.493(3)	S2−O21	1.451(2)
C7−O2	1.305(2)	S2−O22	1.433(1)
C7−N2	1.299(3)	S2−O23	1.427(2)
N2−C8	1.463(3)	O1−HO1	0.86(3)
N2−C9	1.470(3)	O2−HO2	0.76(3)
C10−F11	1.312(3)	O21···HO1	1.74(3)
C10−F12	1.325(2)	O11···HO2	1.82(3)
C10−F13	1.317(3)	O1···O21	2.584(2)
C10−S1	1.812(2)	O2···O11	2.564(2)

Table 4. Molecular planes and interplanar angles (°).

No. of plane	Atoms included	Max. deviation of atoms/Å	Interplanar angles/°
1	N1, C3, O1, C4	0.001 (C3)	1–3: 2.0
2	N2, C7, O2, C6	0.008 (C7)	2–4: 5.0
3	C1, C2, N1, C3	0.008 (N1)	1–5: 92.3
4	C8, C9, N2, C7	0.021 (N2)	2–5: 96.8
5	C4, C5, C6	0	1–2: 62.5

Distances of atoms from planes/Å
1 HO1, −0.009(32); O21, 0.031(2), C5, 1.412(2)
2 HO2, −0.097(29); O11, −0.001(2); C5, 1.405(2)
5 C3, −0.064(2); C7, 0.160(2)

Torsional angles/°

C1 N1 C3 O1	−2.5	C4 C5 C6 C7	173.4
C1 N1 C3 C4	177.2	C5 C6 C7 O2	−79.9
C2 N1 C3 O1	179.0	C5 C6 C7 N2	98.5
C2 N1 C3 C4	−1.2	N2 C7 O2 HO2	172.5
N1 C3 O1 HO1	179.3	C6 C7 N2 C8	−2.0
N1 C3 C4 C5	88.9	O2 C7 N2 C8	176.5
O1 C3 C4 C5	−91.3	C6 C7 N2 C9	173.9
C3 C4 C5 C6	177.3	O2 C7 N2 C9	−7.6

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stead of H⁺)[4,13,14] are listed. As can be seen from this table, the carbonyl bond is lengthened from 1.23–1.24 Å to 1.25–1.27 Å upon partial protonation (very strong hydrogen bonding) and then further to 1.29–1.31 Å when fully protonated. The opposite trend is observed in the C(O)−N bond.[11,13] Angle N−C−O also increases upon protonation.

There still seems to be some controversy with respect to the site of protonation in amides.[15-17] Structural (see Table 5) and spectral data are clearly in favour of protonation at the most basic site: the amide oxygen atom.[4,19] The resulting cation is then stabilized by delocalization of charge over the O⋯C⋯N moiety, whereas *N*-protonation would put most of the positive charge on nitrogen alone.

Hydrogen bonding. Each of the two protonated amide carbonyl groups forms a hydrogen bond to an oxygen atom of a trifluoromethanesulfonate anion. Both bonds are relatively strong[19] with O1⋯O21 = 2.584(2) and O2⋯O11 = 2.563(2) Å. The corresponding O−H and H⋯O bonds have average values of 0.82 and 1.78 Å, while the average O−H⋯O angle is 166(2)°. In acetamide·
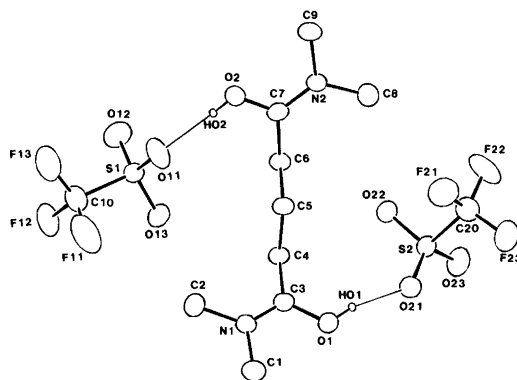

Fig. 1. The structure of the 1:2 adduct between *N,N,N',N'*-tetramethylglutaramide and trifluoromethanesulfonic acid.

HNO₃ a similar hydrogen bond is found with O⋯O = 2.566(4) Å.[13] There, the O−H⋯O angle is 10° larger than in the present investigation.

The anions. Both trifluoromethanesulfonate anions have normal bond lengths and angles.[20] Average bond lengths are: C−S = 1.816, C−F =

Table 5. Bond lengths/Å and angles/° in selected amides and protonated amides.

Amide or protonated amide	N−C	C=O	C=O⋯H⋯X:[a,b] O⋯X	X	N−C(O)−C	N−C−O	C−C−O	Ref.
1 Acetamide (at 85 K)	1.3296(15)	1.2467(13)	2.91	(H)N	116.78(9)	122.40(7)	120.81(10)	5
2 Diethylacetamide	1.330(5)	1.238(5)	2.93	(H)N	116.3(4)	121.9(4)	121.8(4)	7
3 *N,N,N',N'*-Tetramethyl-oxamide	1.317(3)	1.228(3)			118.0(2)	124.2(2)	117.6(2)	8
4 *N,N'*-Bis(2-chlorethyl)-glutaramide	1.38(1)	1.20(1)	2.83	(H)N	116.1(4)	118.6(4)	125.2(5)	9
	1.34(1)	1.23(1)	2.85	(H)N	115.0(4)	122.7(4)	122.3(4)	
5 Bis(acetamide)·HCl	1.3045(10)	1.2654(10)	2.4507(14)*	O=C	119.11(8)	119.67(7)	121.23(8)	10
6 Bis(acetamide)·HBr	1.307(4)	1.264(4)	2.438(5)*	O=C	119.0(3)	119.7(3)	121.3(3)	11
7 Succinic acid diamide·H₂TeBr₆	1.33(3)	1.25(3)	2.45(3)*	O=C	117(2)	121(2)	122(2)	12
	1.31(3)	1.26(3)	2.45(3)*	O=C	119(2)	120(2)	121(2)	
8 Acetamide·HNO₃	1.287(5)	1.292(5)	2.566(4)	ONO₂⁻	121.3(3)	117.6(3)	121.3(3)	13
9 *N,N'*-Dimethyl-acetamide·HCl	1.290(6)	1.303(6)	2.86	Cl⁻	123.0(5)	117.3(5)	119.3(5)	4
10 *N,N,N',N'*-Tetra-methylglutaramide·2HO₃SCF₃	1.295(3)	1.308(2)	2.584(2)	CF₃SO₂O⁻	123.6(2)	116.3(2)	120.1(2)	
	1.299(3)	1.305(2)	2.564(2)	CF₃SO₂O⁻	124.3(2)	116.1(2)	119.6(2)	
11 *N,N*-Dimethyl-(*O*-ethyl)--phenylpropiolamidium tetrafluoroborate	1.315(8)	1.282(7)			121.5(5)	118.5(4)	120.1(4)	14

[a](H)X indicates that the proton resides on X. [b]A star (*) indicates that the proton is shared equally by O and X.

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1.322 and $S-O = 1.453$ Å for oxygen atoms which take part in hydrogen bonding and therefore form significantly longer $S-O$ bonds than the other oxygens. The other $S-O$ bonds have an average length of 1.426 Å.

IR spectra. Recordings in NUJOL shows that the strong $v_{C=O}$ at 1635 cm^{-1} in the parent amide disappears upon protonation and instead a strong absorption at 1690 cm^{-1} is found. This is probably due to C=N stretch, in analogy with spectral assignments for protonated *N,N*-dimethylacetamide.[4]

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