Crystal and Molecular Structure of Carbonohydrazide Sulphate

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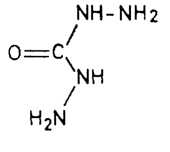
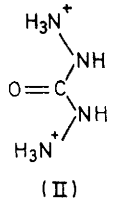
Crystals of the title compound are monoclinic with $a = 10{\cdot}80(1)$, $b = 14{\cdot}60(2)$, $c = 8{\cdot}38(1)$ Å, $\beta = 94{\cdot}3(2)°$, space group $P2_1/c$, $Z = 8$. There are two crystallographically independent stoicheiometric units in the cell. The structure was solved from diffractometric data by direct methods and refined by block-diagonal least-squares to R 0·055 for 1723 observed reflections. The structure consists of diprotonated cations, in a *cis,cis*-conformation and of sulphate anions. The distances and angles in the two independent units are practically equal. The two cations possess an approximate binary axis of symmetry through C–O. Several $>$NH ··· O and $-\overset{+}{N}H_3$ ··· O hydrogen bonds with surrounding anions are formed. The molecular and structural details are very close to those of the thio-analogue, although the latter is orthorhombic.

In the crystalline state the molecule of thiocarbonohydrazide $SC(NH–NH_2)_2$, when neutral (tcaz)[1-3] or monoprotonated (tcazH$^+$)[3] has a *cis,trans*-conformation, *i.e.* with the $-NHNH_2$ groups rotated with respect to the S–C bond, but when it is diprotonated[4,5] it has the *cis,cis*-conformation, *i.e.* with both $-NH{\cdot}NH_2$ groups bent toward the S–C bond. Similar behaviour is observed with carbonohydrazide which has a *cis,trans*-conformation for the neutral molecule (I)[6] and a *cis,cis*-conformation (II) when it is diprotonated, as in the sulphate. We report the crystal structure of the sulphate of (II).


(I)


(II)

EXPERIMENTAL

Preparation.—Colourless crystals were obtained by evaporating an aqueous solution of carbonohydrazide, after addition of dilute sulphuric acid to *ca.* pH 2.

Crystal Data.—$CH_8N_4O_5S$, $M = 188{\cdot}16$. Monoclinic, $a = 10{\cdot}80(1)$, $b = 14{\cdot}60(2)$, $c = 8{\cdot}38(1)$ Å, $\beta = 94{\cdot}3(2)°$, $U = 1317{\cdot}7$ Å^3, $D_c = 1{\cdot}896$, $Z = 8$, $D_m = 1{\cdot}886$, $F(000) = 720$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 275·67 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Unit-cell parameters were determined from rotation and Weissenberg photographs and refined on an automated single-crystal diffractometer.

Intensity Data.—Intensity data were collected on a single-crystal automated Siemens diffractometer, on-line to a Siemens 304 P computer, by use of nickel-filtered Cu-K_α radiation and the ω—2θ scan technique. A rather irregular prism of dimensions *ca.* $0{\cdot}080 \times 0{\cdot}095 \times 0{\cdot}195$ mm^3 was aligned with its [001] axis along the ϕ axis of the diffractometer and all reflections with $2\theta \leqslant 140°$ were collected. Of 2496 independent reflections, 1723 having $I > 2\sigma(I)$ were considered observed and were used in the analysis. Corrections for Lorentz and polarization factors

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[2] F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 392.

[3] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *J.C.S. Perkin II*, 1972, 2116.

[4] A. Braibanti, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 523.

[5] F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, and A. Tiripicchio, *J.C.S. Perkin II*, 1972, 2121.

[6] P. Domiano, M. A. Pellinghelli, and A. Tiripicchio, *Acta Cryst.*, 1972, *B*, **28**, 2495.

were made in the usual way, but no correction was applied for absorption effects. Wilson's method [7] was used to put the structure amplitudes on an absolute scale and to estimate an overall temperature factor; normalized structure factors, $|E_h|$, were then computed.

TABLE 1

Starting set for phases determination

h	k	l	$\|E\|$	
8	6	3	4·14 +	Origin-determining
0	1	7	3·23 +	
9	11	0	3·35 +	
2	4	−6	3·15	a
7	12	1	3·76	b
7	14	−2	3·66	c
1	11	−2	2·75	d

TABLE 2

Final fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

S(1)	1399(1)	3612(1)	2238(1)
S(2)	6370(1)	3794(1)	2096(1)
O(1)	4428(3)	1488(2)	2765(4)
O(2)	9208(3)	1402(2)	2874(4)
O(3)	1835(3)	2671(2)	2615(4)
O(4)	1916(3)	3934(2)	0770(4)
O(5)	1837(3)	4231(3)	3564(4)
O(6)	0020(3)	3620(2)	2086(4)
O(7)	6668(3)	2875(2)	2735(4)
O(8)	7061(3)	3947(2)	0685(4)
O(9)	6728(3)	4506(2)	3315(4)
O(10)	5024(3)	3848(3)	1696(5)
N(1)	5971(4)	0899(3)	1340(5)
N(2)	6387(4)	0356(3)	2688(5)
N(3)	4487(4)	1818(3)	0114(5)
N(4)	3530(3)	2475(3)	0260(5)
N(5)	10,671(4)	0735(3)	1428(5)
N(6)	11,224(4)	0319(3)	2837(5)
N(7)	9214(4)	1661(3)	0217(5)
N(8)	8354(4)	2380(3)	0323(5)
C(1)	4920(4)	1406(3)	1506(6)
C(2)	9689(4)	1283(3)	1614(5)
H(1)	6212(49)	0713(37)	0281(65)
H(2)	6518(48)	0720(35)	3623(63)
H(3)	7131(49)	0064(37)	2292(63)
H(4)	5834(48)	−0071(36)	2816(62)
H(5)	4852(51)	1874(38)	−0732(67)
H(6)	3854(46)	3058(35)	0334(60)
H(7)	2916(46)	2447(36)	−0673(61)
H(8)	3001(50)	2285(38)	1201(67)
H(9)	11,169(53)	0731(40)	0322(69)
H(10)	11,284(49)	0726(37)	3667(65)
H(11)	11,961(53)	0104(40)	2769(69)
H(12)	10,689(49)	−0215(37)	3055(65)
H(13)	9657(52)	1517(39)	−0745(69)
H(14)	8686(45)	2904(34)	0374(58)
H(15)	7792(45)	2336(34)	−0492(59)
H(16)	8014(46)	2266(35)	1112(61)

Structure Determination and Refinement.—The structure was solved by direct methods using the Multan program.[8] Only normalized structure factors >1·41 were used in the phase determination. Since reflections with h odd were very weak (only 48 of 402 with $E > 1{\cdot}41$), this whole class of reflections were completely eliminated before the end of the convergence. The $|F_h|$ values were therefore normalized again by applying a different scale factor to h even and to h odd sets so as to have $\langle|E^2|\rangle$ 1 for both sets separately. Repeating Σ_2 and 'converge' produced a good starting point (Table 1) and 16 sets of phases for 397 reflections with $E > 1{\cdot}41$ (204 with h even and 193 with h odd) were determined. By use of the set with the highest figures of merit, an E map was computed, which revealed the whole structure excepting the hydrogen atoms. A structure-factor calculation with atomic parameters obtained from this E map gave R 0·275. The structure was refined by block-diagonal least-squares, first with isotropic temperature factors and then with anisotropic thermal parameters; R was reduced to 0·066. At this stage a ΔF map showed all the hydrogen atom positions and when all atoms were refined, R was 0·055. Unit weights were used in all the stages of the refinement.

Atomic scattering factors for sulphur, oxygen, nitrogen, and carbon were taken from ref. 9 and for hydrogen from ref. 10.

Final atomic co-ordinates and the thermal parameters are given in Tables 2 and 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20862 (13 pp., 1 microfiche).†

TABLE 3

Thermal parameters ($\times 10^2$), with estimated standard deviations in parentheses

(*a*) Anisotropic *

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	137(4)	201(4)	178(4)	−15(3)	10(3)	−14(4)
S(2)	142(4)	211(4)	192(5)	−30(4)	27(3)	−33(4)
O(1)	276(15)	309(16)	267(15)	81(13)	75(12)	6(13)
O(2)	280(15)	342(16)	211(14)	80(13)	43(11)	19(13)
O(3)	243(14)	228(14)	309(17)	11(11)	−7(12)	71(12)
O(4)	258(14)	308(15)	201(14)	−13(12)	62(11)	70(12)
O(5)	263(15)	342(17)	297(16)	−119(13)	48(12)	−128(13)
O(6)	144(12)	295(15)	348(17)	−18(11)	9(11)	−47(13)
O(7)	366(17)	236(15)	288(17)	−85(13)	−51(13)	69(13)
O(8)	271(15)	268(15)	222(14)	−9(12)	64(11)	3(12)
O(9)	319(16)	297(16)	299(17)	−152(13)	73(13)	−125(13)
O(10)	147(13)	362(18)	601(23)	−5(13)	4(14)	−201(17)
N(1)	295(19)	272(19)	238(18)	129(15)	26(15)	18(14)
N(2)	208(16)	196(16)	273(19)	39(13)	−12(14)	43(13)
N(3)	296(18)	290(19)	249(19)	135(15)	19(15)	−1(15)
N(4)	167(14)	206(16)	267(18)	59(12)	10(13)	−11(13)
N(5)	210(16)	263(18)	301(19)	83(14)	3(14)	46(15)
N(6)	211(17)	228(17)	267(19)	54(13)	−20(14)	8(14)
N(7)	301(19)	326(20)	261(19)	176(16)	0(15)	−38(15)
N(8)	214(16)	218(17)	290(19)	59(14)	−14(14)	−28(14)
C(1)	188(18)	174(18)	315(22)	8(15)	−39(15)	−12(16)
C(2)	217(18)	213(19)	189(19)	19(15)	−38(14)	−21(15)

(*b*) Isotropic

	B		B
H(1)	354(125)	H(9)	428(139)
H(2)	319(120)	H(10)	350(126)
H(3)	333(125)	H(11)	421(140)
H(4)	325(123)	H(12)	354(129)
H(5)	395(134)	H(13)	411(136)
H(6)	275(113)	H(14)	257(110)
H(7)	291(115)	H(15)	261(110)
H(8)	380(130)	H(16)	299(116)

* In the form: $\exp\left[-0{\cdot}25(h^2a^{*2}B_{11} + \ldots 2klb^*c^*B_{23})\right]$.

All calculations were performed on a CDC 6600 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), with programs by Immirzi.[11]

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1972, Index issue.

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TABLE 4

Diprotonated carbonohydrazide cations, $OC(NH{-}\overset{+}{N}H_3)_2$. Main interatomic bond distances and angles, with estimated standard deviations in parentheses

(*a*) Distances (Å)

C(1)–O(1)	1·222(6)	C(2)–O(2)	1·224(6)
C(1)–N(1)	1·371(7)	C(2)–N(5)	1·347(7)
C(1)–N(3)	1·364(7)	C(2)–N(7)	1·360(6)
N(1)–N(2)	1·425(6)	N(5)–N(6)	1·419(6)
N(3)–N(4)	1·422(6)	N(7)–N(8)	1·409(7)
N(1)–H(1)	0·98(5)	N(5)–H(9)	1·11(6)
N(2)–H(2)	0·95(5)	N(6)–H(10)	0·91(5)
N(2)–H(3)	0·99(5)	N(6)–H(11)	0·86(6)
N(2)–H(4)	0·88(5)	N(6)–H(12)	1·00(5)
N(3)–H(5)	0·84(6)	N(7)–H(13)	0·99(6)
N(4)–H(6)	0·92(5)	N(8)–H(14)	0·84(5)
N(4)–H(7)	0·99(5)	N(8)–H(15)	0·88(5)
N(4)–H(8)	1·05(6)	N(8)–H(16)	0·80(5)

(*b*) Angles (deg.)

N(1)–C(1)–O(1)	123·9(4)	N(5)–C(2)–O(2)	125·0(4)
N(1)–C(1)–N(3)	112·6(4)	N(5)–C(2)–N(7)	113·0(4)
O(1)–C(1)–N(3)	123·5(4)	O(2)–C(2)–N(7)	121·9(4)
C(1)–N(1)–N(2)	115·7(4)	C(2)–N(5)–N(6)	116·4(4)
H(1)–N(1)–C(1)	121·3(32)	H(9)–N(5)–C(2)	122·5(30)
H(1)–N(1)–N(2)	118·3(32)	H(9)–N(5)–N(6)	119·6(30)
N(1)–N(2)–H(2)	111·2(31)	N(5)–N(6)–H(10)	110·9(34)
N(1)–N(2)–H(3)	100·9(31)	N(5)–N(6)–H(11)	115·7(39)
N(1)–N(2)–H(4)	108·4(34)	N(5)–N(6)–H(12)	105·9(31)
H(2)–N(2)–H(3)	116·4(44)	H(10)–N(6)–H(11)	105·9(51)
H(2)–N(2)–H(4)	111·0(46)	H(10)–N(6)–H(12)	112·3(46)
H(3)–N(2)–H(4)	108·2(46)	H(11)–N(6)–H(12)	106·2(50)
C(1)–N(3)–N(4)	115·4(4)	C(2)–N(7)–N(8)	117·1(4)
C(1)–N(3)–H(5)	127·7(38)	C(2)–N(7)–H(13)	116·1(33)
H(5)–N(3)–N(4)	113·4(38)	H(13)–N(7)–N(8)	124·8(33)
N(3)–N(4)–H(6)	110·8(31)	N(7)–N(8)–H(14)	113·5(33)
N(3)–N(4)–H(7)	110·7(30)	N(7)–N(8)–H(15)	108·4(32)
N(3)–N(4)–H(8)	109·1(30)	N(7)–N(8)–H(16)	104·1(37)
H(6)–N(4)–H(7)	108·7(44)	H(14)–N(8)–H(15)	111·7(46)
H(6)–N(4)–H(8)	114·9(44)	H(14)–N(8)–H(16)	111·5(50)
H(7)–N(4)–H(8)	102·3(42)	H(15)–N(8)–H(16)	107·1(48)

DISCUSSION

The crystal structure consists of cations $O{:}C(NH{\cdot}NH_3)_2^{2+}$ in a *cis,cis*-conformation and SO_4^{2-} anions. There are two crystallographically independent formula units (Figure 1, Table 4), which however from the chemical point of view do not show remarkable differences. The transformation from neutral to diprotonated species is associated, as in the thio-analogue, with the change from a *cis,trans*- to a *cis,cis*-conformation. Both steric hindrance between $-\overset{+}{N}H_3$ and >NH of the opposite group, and electrostatic attraction between the $-\overset{+}{N}H_3$ groups and the electron cloud associated with the C–O group combine to stabilize the *cis,cis*-conformation. The two independent cations, as far as the main interatomic angles and distances (Table 4) are concerned, appear to be practically equal. The analysis of the

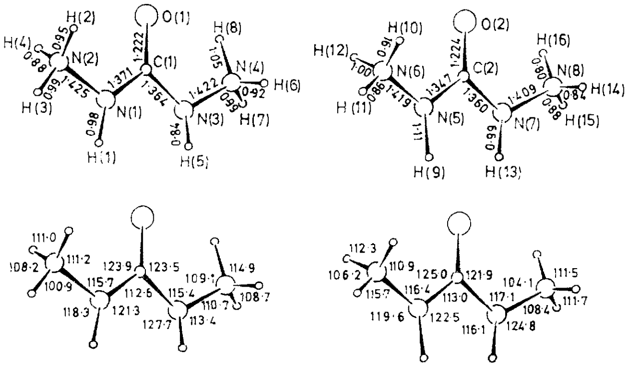

FIGURE 1 The two independent diprotonated *cis,cis*-cations showing the numbering system used in the analysis

TABLE 5

Equations of best least-squares planes in the form $AX + BY + CZ = D$ where $X \equiv x$, $Y \equiv y$, and Z is perpendicular to X,Y. Distances (Å) of relevant atoms from the planes are given

Plane (1): N(1), C(1), O(1), N(3)

$$-0{\cdot}5502X - 0{\cdot}8023Y - 0{\cdot}2315Z = -4{\cdot}8126$$

[N(1) −0·001(4), C(1) 0·003(4), O(1) −0·001(3), N(3) −0·001(4), H(1) 0·24(5), H(5) −0·15(5), N(2) 0·174(4), N(4) −0·225(4)]

Plane (2): N(5), C(2), O(2), N(7)

$$-0{\cdot}5885X - 0{\cdot}7879Y - 0{\cdot}1815Z = -7{\cdot}7989$$

[N(5) 0·008(4), C(2) −0·020(4), O(2) 0·004(3), N(7) 0·007(4), H(9) −0·18(6), H(13) 0·00(6), N(6) −0·027(4), N(8) −0·285(4)]

TABLE 6

Internal rotation angles, ψ, of the hydrazide groups

(*A*) $N(1)H{\cdot}\overset{+}{N}(2)H_3$			(*B*) $N(3)H{\cdot}\overset{+}{N}(4)H_3$			(*C*) $N(5)H{\cdot}\overset{+}{N}(6)H_3$			(*D*) $N(7)H{\cdot}\overset{+}{N}(8)H_3$		
Plane	Atoms	ψ/deg.	Plane	Atoms	ψ/deg.	Plane	Atoms	ψ/deg.	Plane	Atoms	ψ/deg.
(*a*)	C(1), N(1), N(2)	0	(*a*)	C(1), N(3), N(4)	0	(*a*)	C(2), N(5), N(6)	0	(*a*)	C(2), N(7), N(8)	0
(*b*)	N(1), N(2), H(2)	55·96	(*b*)	N(3), N(4), H(8)	31·06	(*b*)	N(5), N(6), H(10)	42·09	(*b*)	N(7), N(8), H(16)	30·7
(*c*)	N(1), N(2), H(3)	179·97	(*c*)	N(3), N(4), H(7)	142·95	(*c*)	N(5), N(6), H(11)	162·74	(*c*)	N(7), N(8), H(15)	144·47
(*d*)	H(1), N(1), N(2)	204·05	(*d*)	H(5), N(3), N(4)	199·42	(*d*)	H(9), N(5), N(6)	166·09	(*d*)	H(13), N(7), N(8)	196·47
(*e*)	N(1), N(2), H(4)	293·64	(*e*)	N(3), N(4), H(6)	263·61	(*e*)	N(5), N(6), H(12)	280·06	(*e*)	N(7), N(8), H(14)	269·23
Rotation (deg.) from (+)-synclinal conformation											
	ψ_b −60	−4·04		ψ_b −60	−28·94		ψ_b −60	−17·91		ψ_b −60	−29·30
	ψ_c −180	−0·03		ψ_c −180	−37·05		ψ_c −180	−17·26		ψ_c −180	−35·53
	ψ_e −300	−6·36		ψ_e −300	−36·39		ψ_c −300	−19·94		ψ_e −300	−30·77
	$\Delta\psi_{av.}$	−3·48		$\Delta\psi_{av.}$	−34·30		$\Delta\psi_{av.}$	−18·37		$\Delta\psi_{av.}$	−31·86
Interplanar angles/deg.											
	(*e*)–(*b*)	122·32		(*e*)–(*b*)	127·45		(*e*)–(*b*)	122·03		(*e*)–(*b*)	121·47
	(*e*)–(*c*)	113·67		(*e*)–(*c*)	120·66		(*e*)–(*c*)	117·32		(*e*)–(*c*)	124·76
	(*c*)–(*b*)	124·01		(*c*)–(*b*)	111·89		(*c*)–(*b*)	120·65		(*c*)–(*b*)	113·77

TABLE 7

Dimensions of the carbonohydrazide molecule (caz) in different crystals

(*a*) Distances (Å)

	C–O	C–N(1)	C–N(3)	N(1)–N(2)	N(3)–N(4)
caz [a]	1·242(2)	(*t*) 1·349(2) [b]	(*c*) 1·350(2)	(*t*) 1·417(3)	(*c*) 1·416(2)
$(cazH_2)SO_4$ [d]	1·222(6)	(*c*) 1·371(7)	(*c*) 1·364(7)	(*c*) *1·425(6)* [c]	(*c*) *1·422(6)*
	1·224(6)	(*c*) 1·347(7)	(*c*) 1·360(6)	(*c*) *1·419(6)*	(*c*) *1·409(7)*

(*b*) Angles (deg.)

	O–C–N(1)	O–C–N(3)	N(1)–C–N(3)	C–N(1)–N(2)	C–N(3)–N(4)
caz [a]	(*t*) 121·1(1)	(*c*) 122·4(1)	116·4(2)	(*t*) 121·6(1)	(*c*) 121·2(2)
$(cazH_2)SO_4$ [d]	(*c*) *123·9(4)*	(*c*) *123·5(4)*	112·6(4)	(*c*) *115·7(4)*	(*c*) *115·4(4)*
	(*c*) *125·0(4)*	(*c*) *121·9(4)*	113·0(4)	(*c*) *116·4(4)*	(*c*) *117·1(4)*

[a] Ref. 6. [b] (*c*) Groups *cis* with respect to O:C:; (*t*) groups *trans* with respect to O:C:. [c] Italicized values are for protonated groups $\cdot NH\cdot\overset{+}{N}H_3$. [d] Present work.

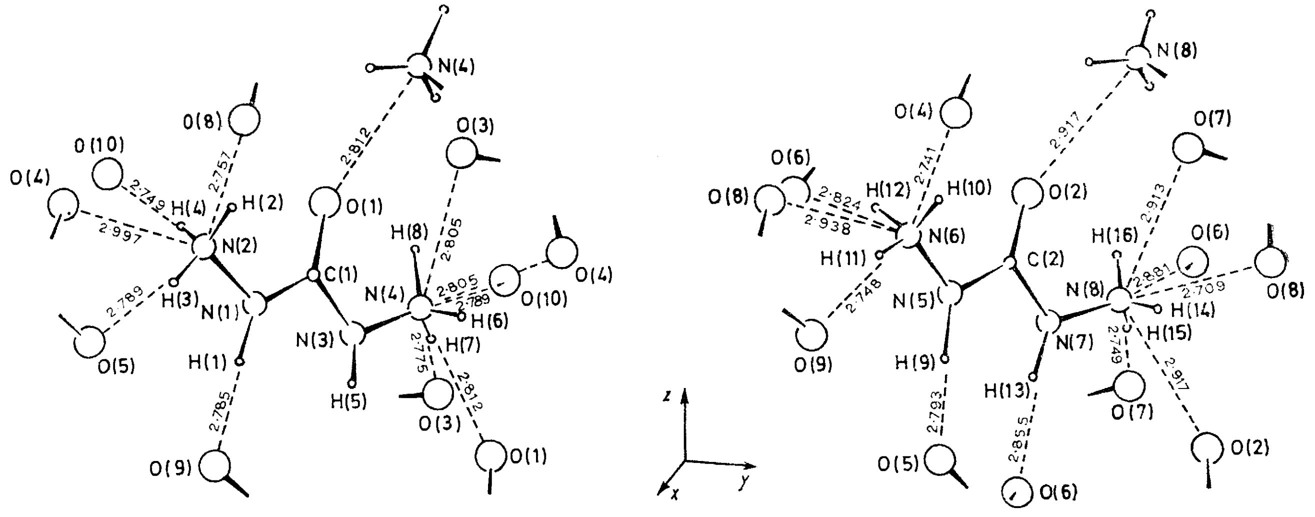

FIGURE 2 Environment of the two diprotonated *cis,cis*-cations

planarity of the two molecules confirms that the ureide group $\mathrm{O{-}C}\genfrac{}{}{0pt}{}{\diagup\mathrm{N}}{\diagdown\mathrm{N}}$ is planar with some π conjugation in it and constitutes the rigid portion of the molecule, the terminal $-\overset{+}{N}H_3$ groups being relatively loose. In fact the deviations from the best planes through the ureide groups (Table 5) show that N(2) and N(4) in one molecule are on opposite sides of the plane through N(1), C(1), O(1), N(3), while N(6) and N(8) in the other molecule are bent toward the same side of the plane through N(5), C(2), O(2), N(7). Some further small differences are shown by the rotation angles around the N–N bonds (Table 6). The rotation from a (+)-synclinal conformation are *ca.* —3 for N(2), —34 for N(4), —18 for N(6), and —32° for N(8); these rotations are associated with distances H(2) · · · O(1) 2·57, H(8) · · · O(1) 2·27, H(10) · · · O(2) 2·49, and H(16) · · · O(2) 2·27 Å. These short hydrogen–oxygen distances are not however indicative of intramolecular hydrogen bonding as shown by the rather large values of the H–N · · · O angles [H(2)–N(2) · · · O(1) 72·8, H(8)–N(4) · · · O(1) 56·6, H(10)–N(6) · · · O(2) 67·7, and H(16)–N(8) · · · O(2) 51·6°], but they indicate an electrostatic attraction of the positive charge of $-\overset{+}{N}H_3$ by the negative charge of the C=O group.

The comparison of bonds angles in caz and $cazH_2^{2+}$ (Table 7) shows that the main variations between the *cis,trans*- and the *cis,cis*-conformations involve the angles N–C–N, O–C–N(1), and C–N–N. These variations are of the same kind as those found in the corresponding thio-species.[5]

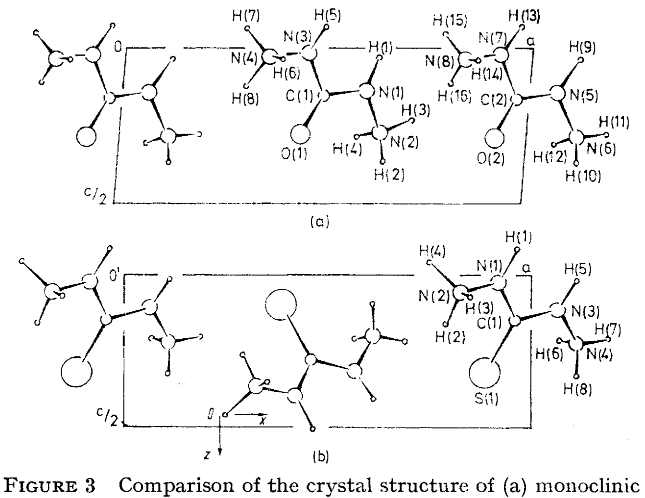

FIGURE 3 Comparison of the crystal structure of (a) monoclinic $(cazH_2)SO_4$ and (b) orthorhombic $(tcazH_2)SO_4$. The origin of (b) has been transferred to 0′ in order to show the agreement between the structures

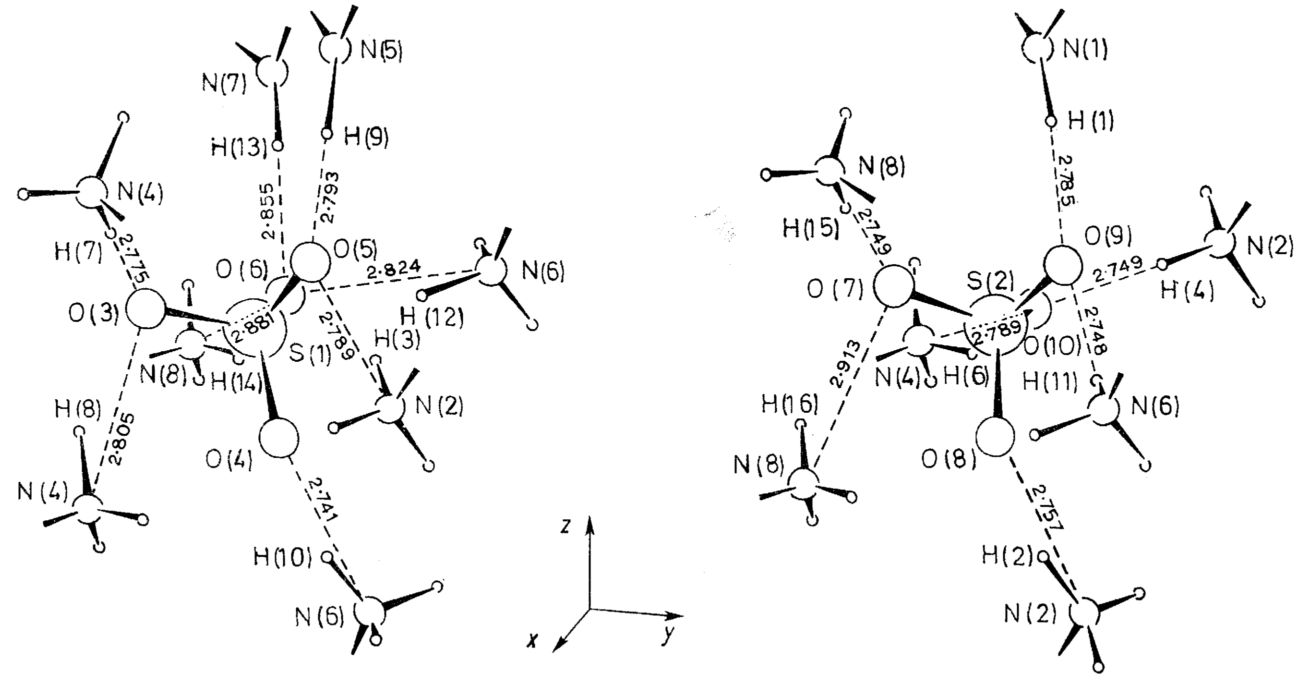

FIGURE 4 Environment of the two sulphate anions

The diprotonated cations are bound *via* hydrogen bonds, N–H · · · O, to the SO_4^{2-} anions (Figure 2). All the hydrogen atoms, excepting H(5), form non-bifurcated hydrogen bonds. The environment of the cation (Table 8) is completed by intermolecular contacts, N · · · O, which, though short, cannot be considered as hydrogen bonds. In fact the angles H(4)–N(2) · · · O(4^{III}) 81·6, H(6)–N(4) · · · O(1^{II}) 53·3, H(6)–N(4) · · · O(4) 61·6, H(12)–N(6) · · · O(8^{VI}) 75·2, H(14)–N(8) · · · O(2^{II}) 47·8, and H(14)–N(8) · · · O(8) 56·6°, are beyond the values acceptable for bent hydrogen bonds. The short contacts, N(4) · · · O(1^{II}) 2·812 and N(8) · · · O(2^{II}) 2·917 Å for the two independent units, arise because the caz molecules are arranged in two zig-zag chains parallel to the *z* axis, successive molecules in the chains being

TABLE 8

Environment of the diprotonated carbonohydrazide cation

(*a*) Hydrogen bonds

(i) Distances (Å)

N(1) · · · O(9^{II})	2·785(6)	H(9) · · · O(5^{IV})	1·69(6)
H(1) · · · O(9^{II})	1·81(5)	N(6) · · · O(4^{V})	2·741(6)
N(2) · · · O(8^{I})	2·757(6)	H(10) · · · O(4^{V})	1·91(5)
H(2) · · · O(8^{I})	1·85(5)	N(6) · · · O(9^{VI})	2·748(8)
N(2) · · · O(5^{III})	2·789(7)	H(11) · · · O(9^{VI})	1·95(6)
H(3) · · · O(5^{III})	1·83(5)	N(6) · · · O(6^{III})	2·824(6)
N(2) · · · O(10^{III})	2·749(7)	H(12) · · · O(6^{III})	1·87(5)
H(4) · · · O(10^{III})	1·89(5)	N(7) · · · O(6^{IV})	2·855(6)
N(4) · · · O(10)	2·789(7)	H(13) · · · O(6^{IV})	1·90(6)
H(6) · · · O(10)	2·00(5)	N(8) · · · O(6^{VII})	2·881(6)
N(4) · · · O(3^{II})	2·775(6)	H(14) · · · O(6^{VII})	2·22(5)
H(7) · · · O(3^{II})	1·79(5)	N(8) · · · O(7^{II})	2·749(7)
N(4) · · · O(3)	2·805(7)	H(15) · · · O(7^{II})	1·87(5)
H(8) · · · O(3)	1·88(6)	N(8) · · · O(7)	2·913(7)
N(5) · · · O(5^{IV})	2·793(6)	H(16) · · · O(7)	2·25(5)

TABLE 8 *Continued*

(ii) Angles (deg.)

H(1)–N(1) · · · O(9^{II})	4·1(31)
N(1)–H(1) · · · O(9^{II})	173·7(49)
H(2)–N(2) · · · O(8^{I})	13·5(31)
N(2)–H(2) · · · O(8^{I})	159·6(46)
H(3)–N(2) · · · O(5^{III})	11·7(31)
N(2)–H(3) · · · O(5^{III})	162·1(48)
H(4)–N(2) · · · O(10^{III})	9·5(34)
N(2)–H(4) · · · O(10^{III})	166·2(50)
H(6)–N(4) · · · O(10)	26·1(31)
N(4)–H(6) · · · O(10)	142·3(44)
H(7)–N(4) · · · O(3^{II})	2·2(30)
N(4)–H(7) · · · O(3^{II})	176·6(47)
H(8)–N(4) · · · O(3)	22·2(30)
N(4)–H(8) · · · O(3)	145·7(45)
H(9)–N(5) · · · O(5^{IV})	2·6(30)
N(5)–H(9) · · · O(5^{IV})	175·6(50)
H(10)–N(6) · · · O(4^{V})	19·8(34)
N(6)–H(10) · · · O(4^{V})	150·8(49)
H(11)–N(6) · · · O(9^{VI})	17·7(38)
N(6)–H(11) · · · O(9^{VI})	154·5(54)
H(12)–N(6) · · · O(6^{III})	12·6(31)
N(6)–H(12) · · · O(6^{III})	160·7(47)
H(13)–N(7) · · · O(6^{IV})	12·1(33)
N(7)–H(13) · · · O(6^{IV})	161·6(49)
H(14)–N(8) · · · O(6^{VII})	32·7(33)
N(8)–H(14) · · · O(6^{VII})	135·4(43)
H(15)–N(8) · · · O(7^{II})	4·0(32)
N(8)–H(15) · · · O(7^{II})	174·1(47)
H(16)–N(8) · · · O(7)	29·0(37)
N(8)–H(16) · · · O(7)	141·1(48)

(*b*) Short intermolecular contacts (Å)

N(8) · · · O(8)	2·709(6)	N(4) · · · O(4)	2·805(7)
N(8) · · · O(2^{II})	2·917(6)	N(4) · · · O(1^{II})	2·812(6)
N(6) · · · O(8^{VI})	2·938(7)	N(2) · · · O(4^{III})	2·997(7)

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I	$x, \frac{1}{2} - y, \frac{1}{2} + z$	V	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
II	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	VI	$2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
III	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	VII	$1 + x, y, z$
IV	$1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$		

related by the c glide. Short contacts N · · · S of the same type are also present in the thio-analogue,[5] which explains the close similarities (Figure 3) observed between the two structures. In fact the cell constants of the two compounds are almost equal and the symmetry operations of the monoclinic group are subgroups of those of the orthorhombic group.

The sulphate anions are practically regular tetrahedra (Table 9). Each oxygen atom is involved in at least one and no more than three hydrogen bonds (Figure 4).

TABLE 9

Sulphate anion: main interatomic distances and angles, with estimated standard deviations in parentheses

(*a*) Distances (Å)

S(1)–O(3)	1·479(4)	S(2)–O(7)	1·472(4)
S(1)–O(4)	1·466(4)	S(2)–O(8)	1·462(4)
S(1)–O(5)	1·482(4)	S(2)–O(9)	1·488(4)
S(1)–O(6)	1·485(6)	S(2)–O(10)	1·469(6)

(*b*) Angles (deg.)

O(3)–S(1)–O(4)	110·0(2)	O(7)–S(2)–O(8)	108·9(2)
O(3)–S(1)–O(5)	109·1(2)	O(7)–S(2)–O(9)	110·4(2)
O(3)–S(1)–O(6)	109·1(2)	O(7)–S(2)–O(10)	108·5(2)
O(4)–S(1)–O(5)	108·3(2)	O(8)–S(2)–O(9)	109·0(2)
O(4)–S(1)–O(6)	111·6(2)	O(8)–S(2)–O(10)	111·3(2)
O(5)–S(1)–O(6)	108·7(2)	O(9)–S(2)–O(10)	108·7(2)

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