

Fig. 2. Stereoscopic projection of the crystal structure along the *b* axis.

dihedral angle with the pyrroline ring is 33.7 (2)°. Fig. 2 shows the crystal structure. There are dimers on centres of symmetry and these dimers build columns, which in turn form sheets of molecules parallel to (100). The distance separating two parallel dimers in the column is 3.480 (4) Å. The intermolecular hydrogen bonds in the dimer are bifurcated ones [2.805 (4) Å]. The distance O2...O2' is also relatively short [2.838 (4) Å; sum of the van der Waals radii: 2.80 Å].

These two atoms are twice bonded by bifurcated hydrogen bonds.

One may conclude that the enol form is also found in solution, because we have an intramolecular hydrogen bond between the hydroxyl and the carbonyl groups, which will stabilize the tautomer found in solution also.

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A Neutron Diffraction Study of Deuterated Semicarbazide Hydrochloride

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Abstract. CD₆N₃O⁺.Cl⁻, *M_r* = 117.5, orthorhombic, *P*2₁2₁2₁, *a* = 7.55 (1), *b* = 13.21 (2), *c* = 4.68 (1) Å, *V* = 466.8 Å³, *Z* = 4, *D_x* = 1.699 g cm⁻³, λ = 1.036 Å, μ_c = 0.45 cm⁻¹, *T* = 298 K, final *R* = 0.033 (on *F*) for 321 independent reflections. The unit-cell volume of deuterated semicarbazide hydrochloride (SEM-DCI) is 466.8 Å³ compared with 463.5 Å³ for semicarbazide hydrochloride (SEM-HCl). The crystal structure is stabilized by a three-dimensional network of N–D...Cl and N–D...O bonds. The present analysis, together with electrical, optical and spectroscopic studies, does not show a ferroelectric phase transition in SEM-DCI and SEM-HCl crystals.

Introduction. Semicarbazide hydrochloride, CH₆N₃O⁺.Cl⁻ (SEM-HCl), containing protonated semicarbazide cations and chloride anions, is reported to undergo two unusually close second-order ferroelectric phase transitions at 292 and 294 K (Rocaries & Boldrini, 1971). The structure of SEM-HCl has been

solved (Nardelli, Fava & Gerdali, 1965) at 294 K, but the H atoms were derived geometrically. No change in crystal symmetry was observed in their X-ray photographic studies at 273 and 294 K. However, the above transitions were supported by marked room-temperature X-ray diffuse scattering. Since the accurate crystal structure and the existence and explanation of the above phase transitions were not clear, we have carried out a thorough study of the structure (Roul, Choudhary, Rajagopal & Sequeira, 1987) and of the optical, spectroscopic and electrical properties (Roul, Choudhary & Rao, 1987) of SEM-HCl. The isotope effect has a major effect on transition temperature (*T_c*), structural parameters and other properties of some hydrogen-bonded ferroelectrics. We have now carried out these studies on the deuterated species SEM-DCI to gain a better understanding of these phenomena.

Experimental. SEM-DCI crystals were grown by slow evaporation of a supersaturated solution of SEM-HCl

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

The equivalent isotropic temperature factor B_{eq} is defined as $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$.

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Cl	0.2544 (3)	0.1398 (2)	0.9647 (6)	2.5 (1)
O	0.7565 (5)	0.0877 (3)	0.8205 (9)	2.0 (2)
N1	0.9277 (5)	0.1608 (3)	0.4792 (9)	2.9 (1)
N2	0.6328 (4)	0.1329 (2)	0.3969 (7)	1.9 (1)
N3	0.4910 (4)	0.0660 (2)	0.4584 (7)	2.1 (1)
C	0.7754 (4)	0.1248 (3)	0.5802 (7)	1.4 (1)
D1	0.0329 (1)	0.1635 (5)	0.5918 (1)	5.9 (8)
D2	0.9449 (7)	0.1898 (4)	0.2958 (8)	6.4 (1.1)
D3	0.6563 (7)	0.1372 (3)	0.1808 (4)	5.3 (1.0)
D4	0.4219 (4)	0.0797 (8)	0.6545 (2)	5.7 (1.4)
D5	0.3996 (4)	0.0794 (7)	0.3122 (7)	5.5 (1.1)
D6	0.5409 (5)	-0.0165 (1)	0.4838 (8)	6.0 (1.4)

and D₂O (99.8%, supplied by the Heavy Water Division, BARC, Trombay, India). SEM-DCI crystallizes as colourless orthorhombic prisms elongated along [001]. The quality and deuteration level of the crystal were improved by recrystallization from D₂O and analyzed by a high-power polarizing microscope and X-ray techniques. A crystal of size 4.1 × 2.2 × 0.5 cm was cut from a larger specimen and mounted with *c* parallel to the ϕ axis of the diffractometer. Neutron diffraction data were recorded using the TDC-312 computer-controlled four-circle diffractometer (Sequeira *et al.*, 1978) at the CIRUS reactor, Trombay, in θ -2 θ mode. Neutron intensities of 321 independent reflections in one octant, $+h$, $+k$, $+l$ ($h=0-7$, $k=0-12$, $l=0-4$), were recorded at a neutron wavelength of 1.036 Å with $\sin\theta/\lambda \leq 0.50 \text{ \AA}^{-1}$. The intensity of one standard reflection measured every 20 reflections was found to vary by only 3%. Unit-cell parameters were refined using the setting angles of 25 strong reflections with $15 \leq \theta \leq 35^\circ$. Systematic absences were consistent with space group $P2_12_12_1$.

Data reduction with *DATRED* (Rajagopal, Srikanta & Sequeira, 1973), which also includes the absorption correction program *ORABS* (Wehe, Busing & Levy, 1962). Maximum and minimum values of the absorption correction were 0.89, 0.84. The reported atomic parameters of SEM-HCl obtained from the neutron diffraction data (Roul, Choudhary, Rajagopal & Sequeira, 1987) were used as the starting parameters for SEM-DCI. The positional and isotropic thermal parameters of all the non-D atoms were first refined, using the full-matrix least-squares program *TRXFLS* [Rajagopal & Sequeira (1977), a modified version of *ORFLS* (Busing, Martin & Levy, 1962)] based on 321 independent reflections [$I \geq 3\sigma(I)$]. The isotropic extinction parameter was also refined. The number of degrees of freedom and structural parameters varied in the final cycle of refinement were 190 and 110 respectively. Positions of all six H atoms in the deuterated crystal were located in a difference Fourier

map using the phases based on neutron non-H-atom positions of SEM-HCl. Full-matrix least-squares refinement (on *F*) with anisotropic temperature factors converged to a final *R* value of 0.033, $wR = 0.069$. A final difference synthesis showed $-0.5 \leq \Delta\rho \leq 0.6 \text{ e \AA}^{-3}$. Fractional coordinates of all atoms are given in Table 1.* The weighting scheme was $w = 1/[\sigma^2 + (0.04y_D)^2]$; $(\Delta/\sigma)_{\text{max}} = 0.04$. Program used: *ORFLS* (Busing, Martin & Levy, 1962). Neutron scattering amplitudes from *International Tables for X-ray Crystallography* (1974).

Discussion. The results of this structural investigation confirm the general structural features of SEM-HCl described earlier (Roul, Choudhary, Rajagopal & Sequeira, 1987). Minor changes of lattice parameters are observed which have increased the unit-cell volume to 466.8 Å³ (SEM-DCI) from 463.5 Å³ (SEM-HCl). A perspective view of the molecule of SEM-DCI, including the atom numbering, is given in Fig. 1. Important bond lengths and valence angles are given in Table 2. The bond-length difference between N2-N3 for the SEM-HCl (1.412 Å) and SEM-DCI (1.417 Å) crystals was found to be very small (0.005 Å) in this three-dimensional network of N-D...Cl and N-D...O bonds. The double-bond character of C-N2 is reflected in a trigonal configuration at N2, with complete coplanarity of non-H atoms in both hydrogenated and deuterated crystals. The carbazide molecule is non-planar and highly distorted. The interaction between organic cations and chloride anions occurs mainly through the H/D atoms bonded to the terminal N3. A packing diagram for the deuterated crystals is given in Fig. 2. It has been observed that bond lengths and valence angles of SEM-HCl change significantly on deuteration.

A three-dimensional network of N-D...Cl and N-D...O bonds stabilizes the molecular structure of SEM-DCI. Relevant data for both the hydrogenated and the deuterated crystals are given in Table 2. It has been observed that the effect of deuteration on

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44828 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

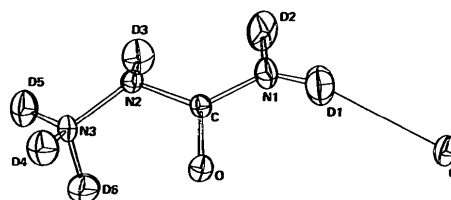


Fig. 1. Perspective view of the SEM-DCI molecule.

Table 2. Comparison of bond lengths (Å), bond angles (°) and hydrogen-bond geometry (Å, °) for SEM-DCI and SEM-HCl with *e.s.d.*'s in parentheses

	SEM-DCI	SEM-HCl		
Bond lengths				
N1—C	1.329 (6)	1.326 (4)		
C—N2	1.380 (5)	1.382 (4)		
C—O	1.236 (6)	1.234 (4)		
N2—N3	1.417 (4)	1.412 (3)		
Cl—H1	2.437 (1)	2.375 (8)		
N1—H1	0.952 (1)	1.003 (10)		
N1—H2	0.951 (8)	0.987 (11)		
N2—C	1.380 (5)	1.382 (4)		
N2—H3	1.029 (6)	1.020 (10)		
N3—H6	1.160 (8)	1.036 (9)		
N3—H4	1.071 (1)	1.051 (9)		
N3—H5	0.988 (3)	1.033 (11)		
Bond angles				
N2—N3—H4	115.9 (7)	111.2 (4)		
N2—N3—H5	101.0 (0)	106.1 (4)		
N2—N3—H6	111.2 (6)	110.4 (4)		
H4—N3—H5	102.9 (4)	107.1 (5)		
H4—N3—H6	103.2 (2)	110.9 (6)		
H5—N3—H6	117.7 (2)	110.9 (6)		
N3—N2—C	114.5 (3)	114.5 (2)		
C—N2—H3	118.8 (3)	117.7 (4)		
N2—C—N1	115.2 (4)	114.9 (3)		
N2—C—O	120.4 (4)	129.7 (3)		
N1—C—O	124.3 (4)	124.4 (3)		
C—N1—H2	125.6 (1)	121.2 (5)		
C—N1—H1	122.6 (1)	117.8 (5)		
H1—N1—H2	111.7 (4)	120.1 (7)		
N3—N2—H3	125.7 (4)	111.1 (4)		
Hydrogen-bond geometry				
X—H...Y	X—H	H...Y	X—Y	X—H...Y
N1—H1...Cl	a 0.952 (1)	2.437 (4)	3.363 (7)	164.1 (2.7)
	b 1.003 (1)	2.375 (8)	3.356 (8)	166.1 (5)
N1—H2...Cl	a 0.951 (8)	2.879 (4)	3.363 (9)	128.4 (3.7)
	b 0.987 (11)	2.856 (10)	3.356 (8)	132.1 (6)
N2—H3...O	a 1.029 (6)	1.965 (4)	2.272 (8)	153.3 (5.7)
	b 1.020 (10)	1.946 (11)	2.276 (9)	156.6 (6)
N3—H4...Cl	a 1.071 (1)	2.115 (4)	3.123 (7)	163.2 (3.1)
	b 1.051 (9)	2.106 (9)	3.121 (9)	162.1 (5)
N3—H5...Cl	a 0.988 (3)	2.117 (6)	3.123 (8)	164.0 (4.2)
	b 1.033 (11)	2.070 (10)	3.121 (9)	163.1 (6)
N3—H6...O	a 1.066 (8)	2.028 (7)	2.640 (8)	131.9 (6)
	b 1.036 (9)	1.978 (9)	2.643 (7)	138.7 (5)

Notes: (a) SEM-HCl, (b) SEM-DCI.

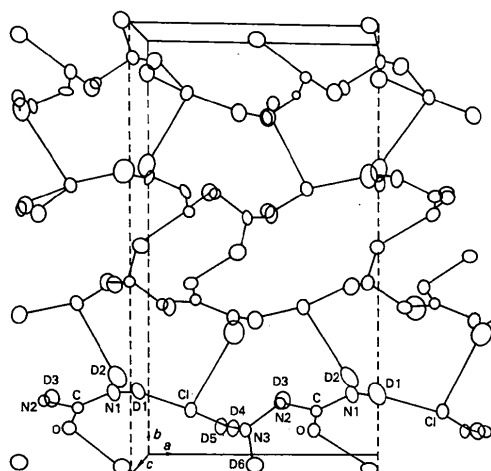


Fig. 2. Packing diagram for deuterated semicarbazide hydrochloride.

hydrogen-bond dimensions is more significant (Ubelohde & Woodward, 1942) than the effect on valence-bond dimensions, consistent with atomic orbital theory. Existing data support the fact that the replacement of H by D does result in elongation (Hadzi, 1959) of hydrogen-bond lengths.

Our dielectric constant and loss measurements on SEM-HCl and SEM-DCI along their various crystallographic axes did not show any anomaly in the temperature range 123–323 K (Roul, Choudhary & Rao, 1987). In addition to this, no hysteresis loop was observed in this range. Our preliminary work on optical and spectroscopic properties does not suggest any phase transition in the compounds. No change in crystal symmetry could be observed in our X-ray data collected at 294 K and neutron data at 298 K in these crystals. Therefore, considering all the above measurements along with neutron structural parameters of both the crystals, we conclude that there is no ferroelectric phase transition in these materials between 123 and 323 K.

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