of the axial over the equatorial isomer of thiacyclohexane 1-oxide (Johnson & McCants, 1964; Martin & Uebel, 1964; Lambert & Keske, 1966) because of attractive van der Waals interaction between the axial O atom and the *syn*-axial hydrogens (Johnson & McCants, 1964; Allinger, Hirsch, Miller & Tyminski, 1969). Although it is reasonable to ascribe the conformational preference in (I) to attractive van der Waals interactions it should be emphasized that the calculations for (I) did not include energy minimization, *e.g.* by rotation about bonds other than C(1)–C(2), or entropy considerations. Furthermore, no attempt was made to calculate electrostatic interactions.

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S-Carboxymethyl-L-cysteine Sulfoxide (Configuration 2*R*:4*R*)

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Abstract. $C_5H_9SO_5N$, orthorhombic, $P2_12_12_1$; $a=4{\cdot}786$ (2), $b=8{\cdot}312$ (1), $c=18{\cdot}914$ (5) Å; $Z=4$, $D_x=1{\cdot}723$, $D_m=1{\cdot}732$ (5) g cm^{-3} (flotation at 21 °C). The structure has been determined by standard Fourier techniques from X-ray diffractometer data and refined by least-squares methods to $R=0{\cdot}035$ for 924 independent reflections. As found by X-ray analysis, the title compound exists as an 'apparent' zwitterion. The cysteine carboxyl and the methyl carboxyl groups of adjacent molecules are involved in a very strong hydrogen bond [O···O 2·449 (3) Å].

Introduction. The title compound and an epimeric sulfoxide were prepared by oxidation of *S*-carboxymethyl-L-cysteine (SCMC). Fractional crystallization from water was used to separate and purify the two epimers. The title compound was the first epimer to crystallize from solution (analysis, calculated for $C_5H_9SO_5N$: 30·77% C, 7·17%N, 4·64% H; composition found: 30·96% C, 6·37% N, 4·78% H). Precession photographs showed *mmm* symmetry. Systematic absences ($h00$, $h=2n+1$; $0k0$, $k=2n+1$; $00l$, $l=2n+1$) observed on the films and verified on the diffractometer

indicated that the space group is $P2_12_12_1$. A colorless ($0{\cdot}44\times0{\cdot}12\times0{\cdot}06$ mm) crystal was mounted on a diffractometer and 943 unique reflections were measured out to $\theta=75°$ with Cu $K\alpha$ X-radiation ($\lambda=1{\cdot}54188$ Å).* A Si(Li) solid-state detector was used to monochromate the diffracted beam (Hubbard, 1973). The θ–2θ scan technique was used with the scan range of $(2{\cdot}2+\tan\theta)°$ and with a scan speed of 4° min^{-1}. 54 intensities were considered to be 'less than' according to the criterion $I(\text{rel})<2\sigma(I)$, where $\sigma(I)=[S+(t_s/t_b)B+0{\cdot}005S]^{1/2}$, where S=scan count (time t_s), and B=background count (time t_b). The 'less than' reflections were excluded from refinement. Intensities were corrected for Lorentz–polarization effects but not for absorption ($\mu=36{\cdot}7$ cm^{-1}). To reduce the effects of decomposition, only one octant of data was collected. Nevertheless, during data collection a steady decrease in each of the three standards occurred. As the decrease was not uniform and the largest change was less than $2\sigma(I)$, no correction was applied. The irradiation also resulted in a steady increase in lattice parameters. Increases as large as 0·1 % occurred during intensity measurements while increases of 0·5% occurred during an extended irradiation period. The cell parameters in the abstract were obtained by least-squares refinement of 20 uniquely-indexed powder-diffraction lines.†

The structure was solved by analysis of the Patterson map and by successive Fourier and difference Fourier maps. The configuration of the cysteine moiety was assumed to be *R* (*rectus*: L-cysteine). The form factors used in the refinement were from *International Tables for X-ray Crystallography* (1968). A full-matrix isotropic least-squares refinement of all atoms except H gave a conventional *R* value of 0·088. All the H atoms were located from difference maps and were added to the model with fixed thermal parameters (isotropic $U=0{\cdot}03$ Å^2). An extinction parameter was not added to the model because of the difficulty of accurately measuring path lengths within the crystal. A full-matrix anisotropic least-squares refinement of the model on all parameters (except hydrogen U's) gave an *R* value of 0·036. To confirm the absolute configuration, anomalous scattering factors for the S atom were introduced, and a further cycle of refinement lowered the *R* value to 0·034. [Refinement of the mirror image (incorrect model) with the cysteine moiety in the D-configuration gave an *R* value of 0·046.] The final conventional *R* value, based on *F*, including 'less than' reflections was 0·035 and $R_w\{=[\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}\}$ was 0·047. The function minimized was $\sum w(|F_o|-|F_c|)^2$ with $w=[\sigma(F_o)]^{-2}$. The final average shift/error was 0·02 with a maximum value of 0·24 for one of the H coordinates. The final correlation matrix indicated that there was no significant coupling of parameters. A final difference electron density map contained no residual peaks in excess of 0·1 e Å^{-3}. All calculations were performed with the X-RAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Tables 1 and 2 list the atomic parameters. Bond distances and angles are shown in Fig. 1. The angles involving H atoms have been omitted. For the H atoms bonded to C and N, the angles range from 103 to 116 (3)°. Fig. 2 shows a stereo view of the packing (*ORTEP*). The distances in this figure correspond to the distances $d_{A\ldots B}$ in Table 3.

Table 2. *Positional parameters* ($\times10^3$) *of the hydrogen atoms with standard deviations in parentheses*

	x	*y*	*z*
H(C2)	1009 (8)	675 (5)	891 (2)
H1(C3)	801 (9)	496 (5)	810 (2)
H2(C3)	499 (9)	597 (5)	814 (2)
H1(C4)	837 (9)	541 (5)	668 (2)
H2(C4)	515 (9)	592 (5)	692 (2)
H1(N)	569 (10)	484 (5)	942 (2)
H2(N)	779 (9)	551 (5)	989 (2)
H3(N)	842 (10)	443 (5)	936 (2)
H(O2···O4)	674 (9)	1042 (5)	917 (2)

Table 1. *Positional* ($\times10^4$) *and thermal* ($\times10^3$) *parameters of the non-hydrogen atoms with standard deviations in parentheses*

Thermal parameters are in the form $T=\exp[-2\pi^2(a^{*2}h^2U_{11}+b^{*2}k^2U_{22}+c^{*2}l^2U_{33}+2a^*b^*hkU_{12}+2a^*c^*hlU_{13}+2b^*c^*klU_{23})]$.

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	8120 (1)	7482 (1)	7540 (1)	30·7 (4)	22·1 (3)	23·9 (3)	−2·0 (3)	0·0 (3)	0·2 (3)
N	7458 (6)	5222 (3)	9442 (1)	37 (1)	19 (1)	22 (1)	4 (1)	−4 (1)	1 (1)
C(1)	6579 (6)	8052 (3)	9181 (1)	29 (1)	24 (1)	18 (1)	5 (1)	−4 (1)	−4 (1)
C(2)	8090 (6)	6551 (3)	8932 (1)	25 (1)	20 (1)	23 (1)	0 (1)	−1 (1)	0 (1)
C(3)	7095 (7)	6030 (3)	8204 (1)	33 (2)	21 (1)	20 (1)	−1 (1)	1 (1)	−1 (1)
C(4)	6858 (7)	6301 (3)	6809 (1)	36 (2)	22 (1)	23 (1)	−2 (1)	0 (1)	1 (1)
C(5)	6535 (6)	7312 (3)	6155 (1)	34 (1)	19 (1)	24 (1)	−1 (1)	4 (1)	−1 (1)
O(1)	4268 (4)	7908 (2)	9458 (1)	29 (1)	31 (1)	34 (1)	2 (1)	5 (1)	−7 (1)
O(2)	7828 (5)	9357 (2)	9053 (1)	38 (1)	19 (1)	47 (1)	3 (1)	6 (1)	2 (1)
O(3)	7716 (4)	8615 (2)	6098 (1)	44 (1)	25 (1)	33 (1)	−9 (1)	2 (1)	3 (1)
O(4)	4884 (6)	6777 (3)	5675 (1)	61 (2)	27 (1)	27 (1)	−13 (1)	−12 (1)	4 (1)
O(5)	11238 (5)	7454 (3)	7516 (1)	29 (1)	51 (1)	41 (1)	−8 (1)	0 (1)	4 (1)

* This weighted average wavelength is on the Deslattes & Henins (1973) scale where $\lambda(\text{Cu } K\alpha_1)=1{\cdot}5405981$ Å.

† A list of structure factors and the observed and calculated powder patterns have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31889 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Interest in SCMC and its air oxidation products, the epimeric sulfoxides and the sulfone, goes beyond studies of protein structure. These products have been found among animal metabolism products of a variety of economically important compounds, such as vinyl chloride, 1,2-dichloroethane and 1,1,2-trichloroethane (Hefner, Watanabe & Gehring, 1975; Green & Hathway, 1975; Yllner, 1971). To better understand the chemistry of these compounds the structure of SCMC sulfone (Hubbard, Mighell, Staffa, Zervos & Konopelski, 1976) and the title compound (SCMC sulfoxide) were determined.

The SCMC sulfoxide molecule (Fig. 1) has two asymmetric centers, one at the C(2) atom and the other at the S atom. The X-ray diffraction study of the first epimer of SCMC sulfoxide established that both asymmetric centers have the *R* (*rectus*) configuration and, therefore, the molecule has the (2*R*:4*R*) configuration. As expected, the oxidation to the sulfoxide did not affect the asymmetric center at C(2) in the L-cysteine moiety in the starting material (SCMC).

The SCMC sulfoxide (2*R*:4*R*) exists as an 'apparent' zwitterion. As indicated in Fig. 1, three H atoms are bonded to the N atom. The exact position of the remaining non-carbon H atom is uncertain. The dotted lines in the figure indicate that this H could not be unambiguously assigned to either the methyl carboxyl O(4) or to the cysteine carboxyl O(2).

The bond lengths and angles of the L-cysteine moiety in SCMC sulfoxide compare closely with those of the zwitterion L-cysteine (Kerr & Ashmore, 1973). For example, the average d_{C-S} in SCMC sulfoxide (2*R*:4*R*) is 1·806 (3) compared to 1·811 (3) Å in L-cysteine; the pair of cysteine d_{C-O} carboxyl distances for the sulfoxide are 1·230 (4) and 1·262 (3) Å compared to 1·238 (3) and 1·256 (3) Å in L-cysteine. Likewise, when the C–S(=O)–C moiety is compared with corresponding parameters in dimethyl sulfoxide (DMSO) (Thomas, Shoemaker & Eriks, 1966) there is reasonably close agreement. In DMSO, it was concluded that the S–O bond was mainly double-bonded covalent instead of semipolar. The same type of bond undoubtedly exists in the title compound. This is consistent with the observation that this O has no intermolecular or intramolecular contact distances with H less than 2·4 Å in a structure in which hydrogen bonding is ubiquitous.

The SCMC sulfoxide molecules are held together by a network of N–H···O hydrogen bonds (Table 3 and Fig. 2). The three H atoms in the ammonium group form hydrogen bonds with the carboxyl O atoms in neighboring molecules. In addition, each SCMC sulfoxide molecule is linked to two adjacent molecules by

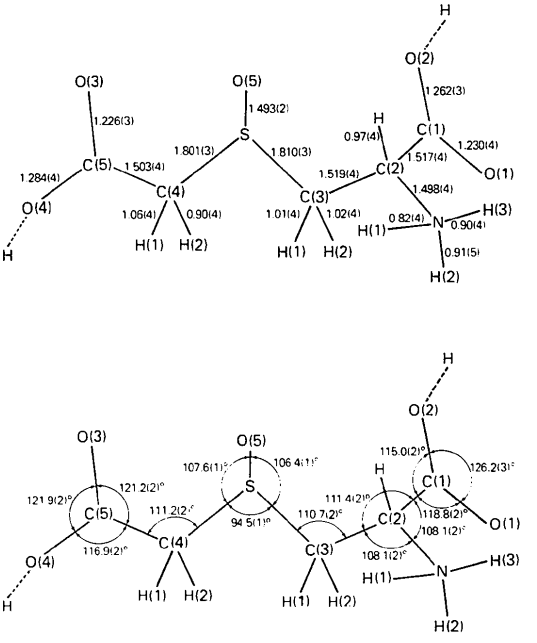

Fig. 1. Bond lengths and angles of SCMC sulfoxide (2*R*:4*R*).

Table 3. *Potential hydrogen-bond distances and angles*

A–H···*B*–*C*	d_{A-H}	$d_{H\cdots B}$	$d_{A\cdots B}$	∠*A*–H···*B*	∠H···*B*–*C*
O(2)–H·····O(4)^{i}—C(5)^{i}	1·04 (4) Å	1·41 (4) Å	2·449 (3) Å	176 (4) °	118 (2) °
N—H(1)···O(3)^{ii} –C(5)^{ii}	0·91 (5)	2·16 (4)	2·994 (4)	153 (4)	96 (1)
N—H(2)···O(1)^{iii}–C(1)^{iii}	0·90 (4)	1·93 (4)	2·737 (3)	148 (3)	122 (1)
N—H(3)···O(3)^{iv} –C(5)^{iv}	0·82 (4)	2·16 (4)	2·857 (4)	144 (4)	135 (1)

Symmetry code

(i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$ (iii) $\frac{1}{2}+x, \frac{3}{2}-y, 2-z$

(ii) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$ (iv) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$

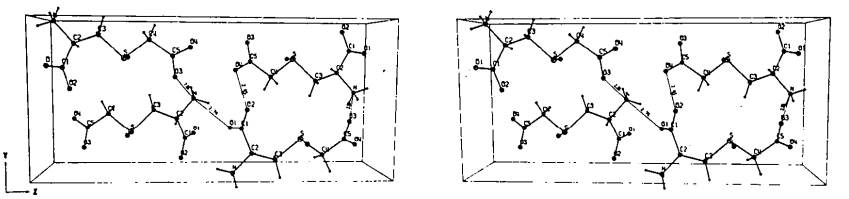

Fig. 2. Steroscopic projection of the structure along *x*.

two, symmetry-equivalent, very short hydrogen bonds [$d_{O\cdots O}$=2·449 (3) Å]. This distance is shorter than the corresponding distance in such neutral dicarboxylic acids as the SCMC sulfone (Hubbard, Mighell, Staffa, Zervos & Konopelski, 1976) and glutamic acid (neutron diffraction study by Lehmann, Koetzle & Hamilton, 1972) in which the O···O distances are 2·504 (5) and 2·519 (2) Å respectively.

The two C–O distances in the C(5) carboxyl of the SCMC sulfoxide are 1·284 (4) and 1·226 (3) Å, the first slightly shorter than and the second slightly longer than expected for a protonated carboxyl group. For example in the glutamic acid zwitterion the C(5) carboxyl is protonated and these distances are 1·312 (2) (C–OH) and 1·219 (2) Å (C=O). Similarly, in SCMC sulfone the C(5) carboxyl was protonated [d_{C-O}= 1·316 (5) and 1·218 (6) Å]. The more nearly equal C–O distances in SCMC sulfoxide (2*R*:4*R*) are indicative of a change from a fully protonated carboxyl group. This hypothesis is further supported by the least-squares position for the H atom in the very short [O···O] hydrogen bond. The H atom unexpectedly refines to a position slightly nearer O(2) (4σ from the O···O midpoint) of the cysteine carboxyl group. The above observations seem to indicate that the C(5) carboxyl may not be protonated, but rather that the H atom could lie at the center of the O···O bond. This is not unusual for very short hydrogen bonds (Hamilton & Ibers, 1968).

Whether the term zwitterion is appropriate for the title compound depends on the definition of zwitterion. Consider the results of the neutron diffraction study on the monocarboxylic amino acids tyrosine and tyrosine.HCl (Frey, Koetzle, Lehmann & Hamilton, 1973). Tyrosine is considered a zwitterion because the carboxyl group is not protonated, but tyrosine.HCl is not considered a zwitterion because the carboxyl group is protonated. In the SCMC sulfoxide (2*R*:4*R*), if the H is in the middle of the O···O strong hydrogen bond, the carboxyl group in the cysteine moiety would be half-protonated; thus the SCMC sulfoxide molecule could be defined either as a zwitterion or not.

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Dérivés de l'Amino-2 Diphénylsulfure. I. Le Maléate de *N*-(Diméthylammonio-3 propyl) Amino-2 Chloro-4 Diphénylsulfure

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(*Reçu le* 26 *avril* 1976, *accepté le* 18 *mai* 1976)

Abstract. $(C_{17}H_{22}N_2SCl)^+(C_4O_4H_3)^-$, monoclinic, $C2/c$, $Z=8$; $a=36{\cdot}41$ (1), $b=5{\cdot}783$ (3), $c=21{\cdot}089$ (8) Å, $\beta=93{\cdot}28$ (7)°; $R=0{\cdot}074$; 3204 observed reflexions. The angle between the two ring planes is 101·3°.

Introduction. Cette étude entreprise dans notre laboratoire a pour objet (dans un premier temps) de déterminer la configuration spatiale de molécules dérivés de l'amino-2 diphénylsulfure. Un grand nombre de ces composés a été synthétisé au Laboratoire de Chimie Organique et Pharmacie Chimique (U.E.R. de Pharmacie) de Lille par D. Bar, M. Debaert et C. Baert. On peut les considérer comme des phénothiazines dans lesquelles le noyau médian serait ouvert au niveau de l'atome d'azote, anihilant ainsi la semi-rigidité de la molécule de phénothiazine. Dans cet ordre d'idée la molécule étudiée dans le présent article, appelée CB7, est l'homologue de la chlorpromazine.