

## The Structures of 4,4'-Dichloro-3,3'-ethylenebis-sydnone and 3,3'-Ethylenebis-sydnone

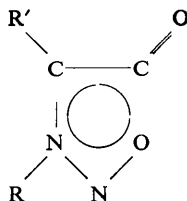
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The crystal structures of 4,4'-dichloro-3,3'-ethylenebis-sydnone (I) and 3,3'-ethylenebis-sydnone (II) have been determined by Fourier and full-matrix least-squares methods. Diffraction data (Cu  $K\alpha$ ) were obtained by use of a Picker automatic diffractometer. Crystals of I are orthorhombic with  $a = 13.109$  (6),  $b = 21.863$  (5),  $c = 6.747$  (3) Å, space group  $Pbca$ , with eight molecules per unit cell. Crystals of II are orthorhombic,  $a = 17.397$  (3),  $b = 7.364$  (4),  $c = 12.582$  (6) Å, space group  $Fdd2$ , with eight molecules per unit cell.  $R$  for I (1312 reflections) is 0.042, and  $R$  for II (449 reflections) is 0.024. Bond distances and angles were corrected for anisotropic thermal motion effects. Estimated standard deviations in bond distances not involving hydrogen are 0.004–0.006 Å for I and 0.002–0.003 Å for II. Average bond distances in the sydnone ring are O–N, 1.39; N–N, 1.32; N–C, 1.34; C–C, 1.40; C–O, 1.41 Å. The carbonyl C–O distance is 1.22 Å. The angle C–C=O is 136° and the angle O–C=O is 120°. The C–Cl distance in I is 1.68 Å. All bonds involving ring atoms are coplanar.

The formulation



is proposed as the best single formula representation of a sydnone.

### Introduction

Sydnes are the products of dehydration of *N*-nitroso- $\alpha$ -amino acids, named after the site of their discovery at the University of Sydney (Earl & Mackney, 1935). Since the early realization that the bicyclic structure I (Fig. 1) was unlikely, the sydnes along with similar substances have been classed as 'mesoionic' compounds (Baker & Ollis, 1957) for which no satisfactory covalent cyclic structure can be written which does not involve separation of charge. Of the two most common representations II and III, Baker & Ollis have preferred formula III which emphasizes the aromatic nature of the sydnone ring and reflects the low bond order for the carbonyl group obtained in several molecular orbital calculations which assume a regular  $\sigma$  framework (for leading references see Kier & Roche, 1966).

The inconsistency between this picture and the high carbonyl stretching frequency has been stressed by Yashunskii and co-workers (Ящунский, Васильева & Шейнкер, 1959). The results of the crystal structure determination of 3-*p*-bromophenylsydnone (Fig. 1,  $R = p\text{-BrC}_6\text{H}_4$ ,  $X = \text{H}$ ) by Bärnighausen, Jellinek, Munnik & Vos (1963) are also difficult to reconcile with III, as nothing unusual about the carbonyl C–O distance was noted. However, these workers observed a 'remarkable distortion' of the bond angles around the carbonyl group (the C–C=O angle was reported to be 135.7° and the O–C=O angle 119.2°) and ascribed it to an intermolecular 'charge transfer interaction' between the carbonyl oxygen and a neighboring bromine atom 3.16 Å distant.

It seemed likely to us that the observed distances and angles were inherent properties of the sydnone system rather than being the result of such a relatively weak interaction. In order to gain insight into the nature of the bonding in these 'mesoionic' systems, we undertook the study of some representative sydnes.

We chose for study 4,4'-dichloro-3,3'-ethylenebis-sydnone and 3,3'-ethylenebis-sydnone (Fig. 1,  $R = \text{CH}_2$ ,  $X = \text{Cl}$  or  $\text{H}$  respectively, molecule dimeric), hereafter referred to as Cl-sydnone and H-sydnone respectively. They are solids for which straightforward syntheses have already been published (Daeniker & Druey, 1957), whose aromatic systems are unperturbed

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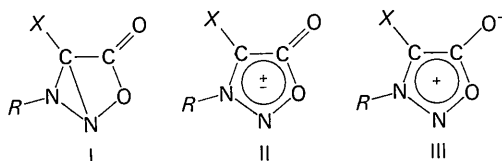


Fig. 1. Conventional structural formulas for sydnes.

by other conjugation, and whose dimeric nature assured either a duplicate determination of the molecular geometry or a symmetry element which might prove useful in the solution of the structure.

Our conclusions on the bonding in the Cl-sydnone have been published in a preliminary communication (Thiessen & Hope, 1967) in which we proposed that sydnones are characterized by delocalization of electrons in the plane of the ring as well as perpendicular to it. Since it could be argued that the large C-C=O angle which we observed in Cl-sydnone might have been affected by an intramolecular interaction between chlorine and carbonyl oxygen we solved and now report the structure of the parent H-sydnone as well.

### Experimental

#### Cl-sydnone

Crystals of Cl-sydnone were grown from an acetone solution. Approximate cell dimensions, crystal system and space group extinction rules were derived from precession and Weissenberg photographs. During the preliminary investigations it was found to be necessary to coat the crystals in order to minimize interaction with the atmosphere, either through evaporation or chemical reaction resulting from X-ray exposure. The coating consisted of a thin layer of Wilhold's white glue ('Glu-Bird') which was applied by dipping the crystal into a drop of the glue thinned with water. [In order to avoid later difficulties and disappointments we have found the following procedure to be of value. A sample crystal is mounted on a precession camera, and continuously exposed to X-rays. Timed exposures of Polaroid film are made at regular intervals, for example once a day; signs of deterioration of the crystal can thereby be detected.]

The crystal used for intensity measurements was shaped to an approximate sphere of diameter 0.17 mm by cutting; its edges were then rounded by dipping the crystal in acetone. Accurate cell dimensions and crystal orientation parameters were obtained from  $\chi$ ,  $\varphi$  and  $2\theta$  angles measured for about ten reflections on a Picker diffractometer equipped with a full-circle goniostat. The cell dimensions resulting from a least-squares cal-

ulation, together with other crystallographic data, are given in Table 1.

The intensities of 2096 reflections accessible below  $2\theta = 160^\circ$  were measured with the diffractometer in automatic mode, using the  $2\theta - \theta$  scan technique with a scan speed of  $2^\circ \text{ min}^{-1}$  and with background measurements taken at both ends of the scan range. Nickel filtered  $\text{CuK}\alpha$  radiation was used with a scintillation detector and pulse height analyzer counting device. The count rate was kept below  $10^4$  counts per second with an automatic attenuator mechanism. Measurements of one check reflection were repeated at regular intervals. The intensity of this reflection showed a slight, gradual decline during the data collection period, at the end of which the intensity amounted to about 92% of its initial value. The instability of the compound under irradiation was the reason for selecting the relatively high scan speed, which in turn resulted in poor counting statistics for a large number of reflections.

The intensities were corrected for Lorentz and polarization effects. The expression

$$s(N) = N^{1/2} + 0.005N$$

was used to obtain an estimated standard deviation for a recorded number of counts. Reflections for which the intensity was less than three times its standard deviation were recorded as 'unobserved', and were not included in subsequent calculations. The resulting number of 'observed' reflections was 1312.

#### H-sydnone

The H-sydnone was found to have a very low solubility in all solvents tested and it was difficult to grow single crystals. The best results were obtained with methanol, but even in that case crystals developed in the form of flakes with dendritic growths. The crystals were found to be stable in air without further precautions.

Crystal data were obtained as described above. A diamond-shaped single crystal with diagonal dimensions 0.37 and 0.20 mm and thickness 0.05 mm was cut from a plate and mounted with its long direction approximately parallel to the goniostat  $\varphi$  axis. With the exception of the scan speed, which was  $1^\circ \text{ min}^{-1}$ ,

Table 1. Crystallographic data for Cl-sydnone and H-sydnone

	4,4'-Dichloro- 3,3'-ethylenebis-sydnone	3,3'-Ethylenebis-sydnone
Cell dimensions (Å)	<i>a</i> 13.109 (6) <i>b</i> 21.863 (5) <i>c</i> 6.747 (3)	17.397 (3) 7.364 (4) 12.582 (6)
Systematically absent reflections	<i>okl</i> $k = 2n + 1$ <i>h0l</i> $l = 2n + 1$ <i>hk0</i> $h = 2n + 1$	<i>hkl</i> not all <i>even</i> or all <i>odd</i> <i>okl</i> $k + l \neq 4n$ <i>h0l</i> $h + l \neq 4n$
Space group	<i>Pbca</i>	<i>Fdd2</i>
Formula units per unit cell	8	8
Calculated density ( $\text{g.cm}^{-3}$ )	1.83	1.63
Observed density ( $\text{g.cm}^{-3}$ )	1.83	1.59

intensity measurements were carried out as for the Cl-sydnone.

All 449 reflections scanned were recorded as 'observed'. Of these, 20 had a net intensity of less than three times the standard deviation.

### Solution and refinement of the structures

#### Cl-sydnone

The structure was solved by the heavy atom method. Positional parameters of the two chlorine atoms in the asymmetric unit were determined from a sharpened three-dimensional Patterson function. A Fourier synthesis calculated by use of the signs of the Cl contributions revealed the positions of all atoms other than hydrogen. The parameters of these atoms, including anisotropic temperature factors, were refined by full-matrix least-squares methods. A difference map computed when the  $R$  index was 0.065 showed the four hydrogen atoms near their calculated positions. Inclusion of the H atoms changed  $R$  to 0.055.

At this point it was apparent that the strongest reflections suffered secondary extinction effects. It was decided to attempt a correction for this by the method of Zachariasen (1963). In order to test the program used, calculations were first done on the  $hk0$  reflections only, for which a very marked improvement was seen in the correlation between observed and calculated structure factors (for example,  $R$  decreased from about 0.05 to 0.031).

When the complete data set was processed in this way we did not find the result to be nearly so convincing. The strong observed structure factors in the  $hk0$  layer were not increased sufficiently, while for the layers  $hk1$  and  $hk2$  an overcompensation took place. It then occurred to us that the low angle  $hk0$  reflections had been measured at the beginning of the run while the lower angle  $hk1$  and  $hk2$  reflections were measured within a relatively short period of time at a later stage, and it appeared possible that the mosaic spread or the crystallite size could have changed as a result of X-ray exposure. Unfortunately, for this data set, only one check reflection, of medium intensity, had been used, so there is no direct evidence for this assumption. (However, in at least one other instance we have observed a very significant increase in intensity with exposure time for an extremely intense check reflection, while a nearby medium intensity reflection showed no systematic drift.)

These considerations led us to carry out the secondary extinction corrections separately on the  $hk0$  reflections in one group and the  $hk1$  and  $hk2$  reflections in another. The remaining layers were left as originally measured. The constant  $C$  (*vide infra*) was determined to be  $5.5 \times 10^{-6}$  for the  $hk0$  reflections, and  $1.3 \times 10^{-6}$  for the  $hk1$  and  $hk2$  reflections.

In the early stages of the least-squares refinement the weighting scheme of Hughes (1941) was used. Following the secondary extinction correction the weights were made proportional to  $1/\sigma^2(F)$ , and a few least-

squares cycles were carried out, refining all positional and thermal parameters, with isotropic temperature factors for hydrogen. The refinement was concluded when the shift was less than one-fifth of the estimated standard deviation for all parameters. The final parameters and their estimated standard deviations are listed in Tables 2, 3, and 4, and a comparison of observed and calculated structure factors is given in Table 8. The value of the  $R$  index is 0.042.

Table 2. Cl-sydnone

Positional parameters (with estimated standard deviations) for Cl, O, N and C.

	$x$	$y$	$z$
O(1)	0.3871 (2)	0.4639 (1)	0.9305 (4)
N(2)	0.4339 (2)	0.4622 (1)	0.7469 (6)
N(3)	0.3652 (2)	0.4369 (1)	0.6305 (5)
C(4)	0.2780 (2)	0.4225 (1)	0.7214 (6)
C(5)	0.2876 (3)	0.4400 (2)	0.9210 (7)
C(6)	0.3900 (3)	0.4330 (2)	0.4181 (7)
Cl(7)	0.1737 (1)	0.3919 (0)	0.6181 (2)
O(8)	0.2321 (2)	0.4393 (1)	1.0642 (5)
O(11)	0.3571 (2)	0.2475 (1)	0.4187 (5)
N(12)	0.3555 (2)	0.3108 (1)	0.4069 (7)
N(13)	0.4511 (2)	0.3255 (1)	0.3969 (5)
C(14)	0.5146 (2)	0.2779 (2)	0.3990 (6)
C(15)	0.4561 (3)	0.2250 (2)	0.4129 (6)
C(16)	0.4786 (3)	0.3908 (2)	0.3751 (8)
Cl(17)	0.6412 (1)	0.2854 (0)	0.3820 (2)
O(18)	0.4721 (2)	0.1703 (1)	0.4200 (5)

#### H-sydnone

With eight molecules per unit cell in space group  $Fdd2$  the molecules are required to have a twofold axis, a fact which greatly facilitated the solution of the structure. Approximate  $x$  and  $y$  coordinates of the 'heavy' atoms were readily derived, mainly from the  $(u, v, 0)$  section of a sharpened Patterson function, and since the geometry of the ring was known, relative  $z$  coordinates could be assigned with reasonable confidence. The observation that the  $0, 0, 12$  reflection was very strong, indicating that in the  $c$  direction atoms are separated by about  $c/12$ , or  $1 \text{ \AA}$ , was also helpful in the estimation of initial  $z$  coordinates. In order to use the equivalent positions as given in *International Tables for X-ray Crystallography* (1952) the orientation of the molecule compatible with these positions was determined by calculating intermolecular distances for the two possible (enantiomeric) orientations of the molecule relative to the  $c$  axis. The parameters arrived at in this manner, together with an overall isotropic temperature coefficient  $B$  of  $4 \text{ \AA}^2$ , gave an  $R$  index of 0.42. The heavy atom parameters, including anisotropic temperature factors were refined by full-matrix least-squares methods, initially with the Hughes weighting scheme. The origin was defined by keeping the  $z$  coordinate of O(1) constant.

The three hydrogen atoms were not included in the calculation until the  $R$  index was about 0.05, at which stage they were placed in calculated positions and assigned a  $B$  of  $4 \text{ \AA}^2$ . The addition of the hydrogen atoms

Table 3. Cl-sydnone. Anisotropic thermal parameters and their estimated standard deviations

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O(1)	4.30 (12)	4.14 (13)	4.78 (17)	-0.24 (10)	-0.56 (12)	-0.83 (12)
N(2)	3.36 (13)	3.45 (13)	5.54 (20)	-0.45 (11)	-0.72 (14)	-0.68 (16)
N(3)	2.85 (11)	2.44 (12)	4.72 (18)	0.18 (9)	-0.32 (13)	-0.11 (13)
C(4)	2.50 (13)	2.83 (14)	4.74 (22)	0.10 (12)	-0.02 (15)	-0.16 (16)
C(5)	3.60 (16)	2.81 (15)	5.20 (25)	0.45 (13)	-0.23 (18)	-0.23 (18)
C(6)	3.54 (15)	3.15 (16)	4.42 (24)	0.13 (13)	0.27 (16)	0.33 (19)
Cl(7)	2.66 (3)	4.52 (4)	5.71 (6)	-0.56 (3)	-0.40 (4)	-0.52 (5)
O(8)	5.12 (14)	5.21 (15)	5.19 (17)	0.47 (12)	0.86 (13)	-0.53 (14)
O(11)	3.04 (9)	3.10 (10)	11.43 (25)	-0.18 (10)	1.10 (15)	-0.20 (16)
N(12)	2.70 (12)	3.34 (14)	11.76 (31)	0.01 (10)	0.93 (19)	-0.03 (20)
N(13)	2.78 (11)	3.17 (12)	4.65 (17)	-0.12 (10)	0.36 (14)	-0.34 (14)
C(14)	2.77 (13)	3.52 (15)	4.52 (22)	0.36 (12)	0.21 (16)	-0.26 (17)
C(15)	3.28 (14)	3.68 (16)	4.89 (24)	0.21 (13)	0.20 (17)	-0.02 (19)
C(16)	3.51 (16)	3.32 (16)	5.30 (26)	-0.39 (14)	0.64 (20)	-0.43 (21)
Cl(17)	2.37 (3)	4.92 (5)	13.41 (12)	0.33 (4)	0.16 (6)	-0.43 (7)
O(18)	4.80 (13)	3.11 (11)	7.38 (19)	0.50 (10)	0.63 (15)	0.14 (14)

Table 4. Cl-sydnone. Positional and isotropic thermal parameters (with estimated standard deviations) for the H atoms

	$x$	$y$	$z$	$B$
H(9)	0.3202 (26)	0.4210 (15)	0.3493 (54)	2.28 (90)
H(10)	0.4040 (26)	0.4760 (17)	0.3754 (56)	0.64 (94)
H(19)	0.5341 (27)	0.3982 (17)	0.4628 (58)	2.34 (99)
H(20)	0.4957 (28)	0.3935 (17)	0.2327 (58)	2.04 (99)

lowered  $R$  to 0.035 without refinement. About ten high intensity reflections showed obvious symptoms of secondary extinction. An attempt to correct for this effect gave quite satisfactory results (with  $C=1.3 \times 10^{-6}$ ) for all reflections with the exception of 022, where  $F_{\text{obs}}$  was about 7% less than  $F_{\text{calc}}$ . This reflection was given zero weight in subsequent calculations. The final stages of the least-squares refinement were carried out with weights for  $\Delta F$  proportional to  $1/\sigma(F)$ . The final shifts were all less than one-fifth of the corresponding standard deviations. The final parameters and their estimated standard deviations are given in Tables 5, 6, and 7. A comparison of observed and calculated structure factors is given in Table 9. The value of the  $R$  index is 0.024.

Table 5. H-sydnone. Positional parameters (with estimated standard deviations) for O, N and C

	$x$	$y$	$z$
O(1)	0.1515 (1)	0.2273 (2)	0.3300 (0)
N(2)	0.1250 (1)	0.1430 (3)	0.4204 (2)
N(3)	0.0507 (1)	0.1695 (2)	0.4171 (2)
C(4)	0.0260 (1)	0.2633 (3)	0.3334 (2)
C(5)	0.0908 (1)	0.3067 (3)	0.2729 (2)
C(6)	0.0042 (1)	0.1014 (3)	0.5064 (2)
O(8)	0.1042 (1)	0.3902 (3)	0.1918 (2)

### Computing procedures

All calculations were performed on an IBM 7044 computer, for the most part using programs listed elsewhere (Hope & Christensen, 1968).

The least-squares program minimizes the quantity  $S = \sum w(K \cdot F_o - G |F_c|)^2$  by a full-matrix routine.  $G$  is

one of the adjustable parameters, which is reset to its original value by changing  $K$  after each cycle. Estimated standard deviations were obtained from the expression  $(a_{ii} S/m)^{1/2}$ , where  $a_{ii}$  is the diagonal element in the inverse normal equation matrix, and  $m$  is the difference between the number of observations and the number of parameters adjusted.

The isotropic temperature factor is of the form  $\exp(-B \sin^2 \theta/\lambda^2)$ , and the anisotropic is of the form  $\exp(-B_{11}a^*h^2/4 - B_{22}b^*k^2/4 - B_{33}c^*l^2/4 - B_{12}a^*b^*hk/2 - B_{13}a^*c^*hl/2 - B_{23}b^*c^*kl/2)$ . The atomic form factors were those given by Hanson, Herman, Lea & Skillman (1964). The  $R$  index is defined by  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

The secondary extinction correction program, written by A.T. Christensen, applies the correction in the form  $F_{\text{corr}} = F_{\text{obs}} (1 + C\beta J_{\text{obs}})^{1/2}$  (Zachariasen, 1963), where  $C$  is a constant, and  $\beta$  equals  $2(1 + \cos^4 2\theta)/$

$(1 + \cos^2 2\theta)^2 \cdot \frac{dA^*/d\mu r}{dA_o^*/d\mu r}$ . For Cl-sydnone the values used

for  $\frac{dA^*}{dA_o^*}$  were those for a sphere of diameter 0.17 mm,

while for H-sydnone a constant value of 1.0 was used.

### Description of the structures

Packing diagrams of the crystal structures of Cl-sydnone and H-sydnone are presented in Figs. 2 and 3, and molecular geometry parameters are given in Figs. 4 and 5. The uncorrected distances and angles were calculated from the positional parameters listed in Tables 2, 4, 5, and 7, while corrected distances and angles

Table 6. H-syndone. Anisotropic thermal parameters and their estimated standard deviations

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O(1)	2.81 (5)	4.25 (7)	4.23 (7)	-0.01 (5)	0.63 (6)	0.22 (6)
N(2)	2.89 (7)	4.22 (8)	4.26 (10)	0.51 (6)	0.12 (7)	0.66 (7)
N(3)	2.60 (6)	2.57 (6)	3.16 (7)	-0.05 (5)	0.03 (6)	-0.25 (6)
C(4)	2.68 (6)	3.60 (9)	3.74 (10)	-0.29 (7)	-0.33 (7)	0.42 (8)
C(5)	3.21 (7)	3.64 (8)	3.23 (9)	-0.71 (7)	-0.20 (7)	-0.21 (7)
C(6)	3.47 (8)	3.05 (8)	2.96 (8)	-0.21 (7)	0.36 (7)	-0.23 (7)
O(8)	4.96 (9)	6.46 (10)	3.53 (7)	-1.90 (8)	-0.31 (6)	1.25 (7)

Table 7. H-syndone. Positional and isotropic thermal parameters (with estimated standard deviations) for the H atoms

	$x$	$y$	$z$	$B$
H(7)	-0.0276 (18)	0.2891 (41)	0.3290 (24)	3.59 (69)
H(9)	-0.0446 (13)	0.1552 (28)	0.5007 (17)	1.16 (45)
H(10)	0.0313 (14)	0.1288 (33)	0.5681 (19)	1.57 (52)

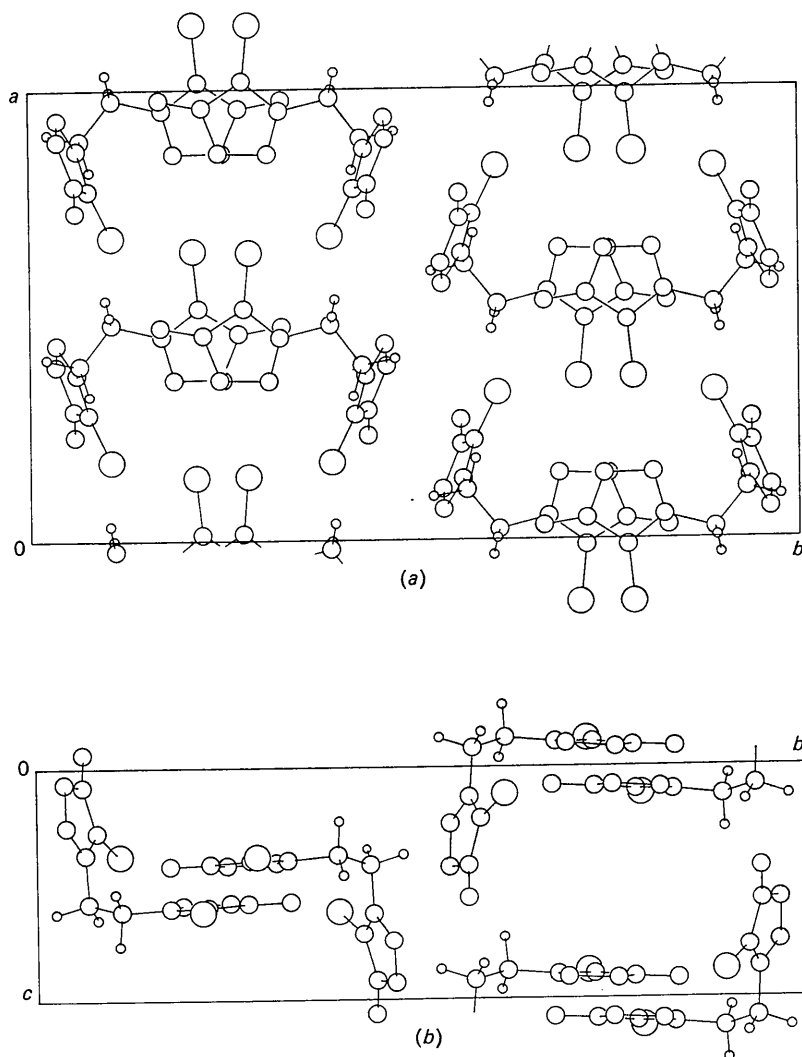
Fig. 2. (a) Projection of the structure of Cl-syndone along the  $c$  axis. (b) Projection of part of the structure along the  $a$  axis. Only molecules related through the  $b$  and  $c$  glides are shown.

Table 8. Cl-sydnone. Observed and calculated structure factors  
The three columns in each group list k, 10F<sub>o</sub> and 10F<sub>c</sub>.

<p>0 0 0 L 0 1 146 -428 4 523 519 6 2012 1380 8 1482-1468 10 45 -29 12 418 -6438 14 470 -641 18 798 781 20 188 -190 22 293-286 24 148-133 26 14 52</p>	<p>14 112 -107 16 385 379 20 76 -64 24 252 -189 28 94 91 32 127 203 36 136 -134 40 115 -106 44 128 -122 48 218 175 52 376 72 56 53 -64 60 189 -187 64 147 -149 68 113 112 72 81 78 76 177-177 80 11 112 84 115 -139 88 178-166 92 2 45-53 96 3 763 741 100 1 828 -825 104 2 45-53 108 3 763 741 112 4 228 322 116 21 75 79 120 18 102 102 124 20 66 72 128 19 156 162 132 23 94 91 136 24 56 52 140 17 87 97 144 12 97 112 148 14 85 -93 152 17 173 -173 156 18 112 102 160 20 66 72 164 21 75 79 168 22 80 80 172 23 94 91 176 24 56 52 180 17 87 97 184 12 97 112 188 14 85 -93 192 17 173 -173 196 18 112 102 200 20 66 72 204 21 75 79 208 22 80 80 212 23 94 91 216 24 56 52 220 17 87 97 224 12 97 112 228 14 85 -93 232 17 173 -173 236 18 112 102 240 20 66 72 244 21 75 79 248 22 80 80 252 23 94 91 256 24 56 52 260 17 87 97 264 12 97 112 268 14 85 -93 272 17 173 -173 276 18 112 102 280 20 66 72 284 21 75 79 288 22 80 80 292 23 94 91 296 24 56 52 300 17 87 97 304 12 97 112 308 14 85 -93 312 17 173 -173 316 18 112 102 320 20 66 72 324 21 75 79 328 22 80 80 332 23 94 91 336 24 56 52 340 17 87 97 344 12 97 112 348 14 85 -93 352 17 173 -173 356 18 112 102 360 20 66 72 364 21 75 79 368 22 80 80 372 23 94 91 376 24 56 52 380 17 87 97 384 12 97 112 388 14 85 -93 392 17 173 -173 396 18 112 102 400 20 66 72 404 21 75 79 408 22 80 80 412 23 94 91 416 24 56 52 420 17 87 97 424 12 97 112 428 14 85 -93 432 17 173 -173 436 18 112 102 440 20 66 72 444 21 75 79 448 22 80 80 452 23 94 91 456 24 56 52 460 17 87 97 464 12 97 112 468 14 85 -93 472 17 173 -173 476 18 112 102 480 20 66 72 484 21 75 79 488 22 80 80 492 23 94 91 496 24 56 52 500 17 87 97 504 12 97 112 508 14 85 -93 512 17 173 -173 516 18 112 102 520 20 66 72 524 21 75 79 528 22 80 80 532 23 94 91 536 24 56 52 540 17 87 97 544 12 97 112 548 14 85 -93 552 17 173 -173 556 18 112 102 560 20 66 72 564 21 75 79 568 22 80 80 572 23 94 91 576 24 56 52 580 17 87 97 584 12 97 112 588 14 85 -93 592 17 173 -173 596 18 112 102 600 20 66 72 604 21 75 79 608 22 80 80 612 23 94 91 616 24 56 52 620 17 87 97 624 12 97 112 628 14 85 -93 632 17 173 -173 636 18 112 102 640 20 66 72 644 21 75 79 648 22 80 80 652 23 94 91 656 24 56 52 660 17 87 97 664 12 97 112 668 14 85 -93 672 17 173 -173 676 18 112 102 680 20 66 72 684 21 75 79 688 22 80 80 692 23 94 91 696 24 56 52 700 17 87 97 704 12 97 112 708 14 85 -93 712 17 173 -173 716 18 112 102 720 20 66 72 724 21 75 79 728 22 80 80 732 23 94 91 736 24 56 52 740 17 87 97 744 12 97 112 748 14 85 -93 752 17 173 -173 756 18 112 102 760 20 66 72 764 21 75 79 768 22 80 80 772 23 94 91 776 24 56 52 780 17 87 97 784 12 97 112 788 14 85 -93 792 17 173 -173 796 18 112 102 800 20 66 72 804 21 75 79 808 22 80 80 812 23 94 91 816 24 56 52 820 17 87 97 824 12 97 112 828 14 85 -93 832 17 173 -173 836 18 112 102 840 20 66 72 844 21 75 79 848 22 80 80 852 23 94 91 856 24 56 52 860 17 87 97 864 12 97 112 868 14 85 -93 872 17 173 -173 876 18 112 102 880 20 66 72 884 21 75 79 888 22 80 80 892 23 94 91 896 24 56 52 900 17 87 97 904 12 97 112 908 14 85 -93 912 17 173 -173 916 18 112 102 920 20 66 72 924 21 75 79 928 22 80 80 932 23 94 91 936 24 56 52 940 17 87 97 944 12 97 112 948 14 85 -93 952 17 173 -173 956 18 112 102 960 20 66 72 964 21 75 79 968 22 80 80 972 23 94 91 976 24 56 52 980 17 87 97 984 12 97 112 988 14 85 -93 992 17 173 -173 996 18 112 102 1000 20 66 72 1004 21 75 79 1008 22 80 80 1012 23 94 91 1016 24 56 52 1020 17 87 97 1024 12 97 112 1028 14 85 -93 1032 17 173 -173 1036 18 112 102 1040 20 66 72 1044 21 75 79 1048 22 80 80 1052 23 94 91 1056 24 56 52 1060 17 87 97 1064 12 97 112 1068 14 85 -93 1072 17 173 -173 1076 18 112 102 1080 20 66 72 1084 21 75 79 1088 22 80 80 1092 23 94 91 1096 24 56 52 1100 17 87 97 1104 12 97 112 1108 14 85 -93 1112 17 173 -173 1116 18 112 102 1120 20 66 72 1124 21 75 79 1128 22 80 80 1132 23 94 91 1136 24 56 52 1140 17 87 97 1144 12 97 112 1148 14 85 -93 1152 17 173 -173 1156 18 112 102 1160 20 66 72 1164 21 75 79 1168 22 80 80 1172 23 94 91 1176 24 56 52 1180 17 87 97 1184 12 97 112 1188 14 85 -93 1192 17 173 -173 1196 18 112 102 1200 20 66 72 1204 21 75 79 1208 22 80 80 1212 23 94 91 1216 24 56 52 1220 17 87 97 1224 12 97 112 1228 14 85 -93 1232 17 173 -173 1236 18 112 102 1240 20 66 72 1244 21 75 79 1248 22 80 80 1252 23 94 91 1256 24 56 52 1260 17 87 97 1264 12 97 112 1268 14 85 -93 1272 17 173 -173 1276 18 112 102 1280 20 66 72 1284 21 75 79 1288 22 80 80 1292 23 94 91 1296 24 56 52 1300 17 87 97 1304 12 97 112 1308 14 85 -93 1312 17 173 -173 1316 18 112 102 1320 20 66 72 1324 21 75 79 1328 22 80 80 1332 23 94 91 1336 24 56 52 1340 17 87 97 1344 12 97 112 1348 14 85 -93 1352 17 173 -173 1356 18 112 102 1360 20 66 72 1364 21 75 79 1368 22 80 80 1372 23 94 91 1376 24 56 52 1380 17 87 97 1384 12 97 112 1388 14 85 -93 1392 17 173 -173 1396 18 112 102 1400 20 66 72 1404 21 75 79 1408 22 80 80 1412 23 94 91 1416 24 56 52 1420 17 87 97 1424 12 97 112 1428 14 85 -93 1432 17 173 -173 1436 18 112 102 1440 20 66 72 1444 21 75 79 1448 22 80 80 1452 23 94 91 1456 24 56 52 1460 17 87 97 1464 12 97 112 1468 14 85 -93 1472 17 173 -173 1476 18 112 102 1480 20 66 72 1484 21 75 79 1488 22 80 80 1492 23 94 91 1496 24 56 52 1500 17 87 97 1504 12 97 112 1508 14 85 -93 1512 17 173 -173 1516 18 112 102 1520 20 66 72 1524 21 75 79 1528 22 80 80 1532 23 94 91 1536 24 56 52 1540 17 87 97 1544 12 97 112 1548 14 85 -93 1552 17 173 -173 1556 18 112 102 1560 20 66 72 1564 21 75 79 1568 22 80 80 1572 23 94 91 1576 24 56 52 1580 17 87 97 1584 12 97 112 1588 14 85 -93 1592 17 173 -173 1596 18 112 102 1600 20 66 72 1604 21 75 79 1608 22 80 80 1612 23 94 91 1616 24 56 52 1620 17 87 97 1624 12 97 112 1628 14 85 -93 1632 17 173 -173 1636 18 112 102 1640 20 66 72 1644 21 75 79 1648 22 80 80 1652 23 94 91 1656 24 56 52 1660 17 87 97 1664 12 97 112 1668 14 85 -93 1672 17 173 -173 1676 18 112 102 1680 20 66 72 1684 21 75 79 1688 22 80 80 1692 23 94 91 1696 24 56 52 1700 17 87 97 1704 12 97 112 1708 14 85 -93 1712 17 173 -173 1716 18 112 102 1720 20 66 72 1724 21 75 79 1728 22 80 80 1732 23 94 91 1736 24 56 52 1740 17 87 97 1744 12 97 112 1748 14 85 -93 1752 17 173 -173 1756 18 112 102 1760 20 66 72 1764 21 75 79 1768 22 80 80 1772 23 94 91 1776 24 56 52 1780 17 87 97 1784 12 97 112 1788 14 85 -93 1792 17 173 -173 1796 18 112 102 1800 20 66 72 1804 21 75 79 1808 22 80 80 1812 23 94 91 1816 24 56 52 1820 17 87 97 1824 12 97 112 1828 14 85 -93 1832 17 173 -173 1836 18 112 102 1840 20 66 72 1844 21 75 79 1848 22 80 80 1852 23 94 91 1856 24 56 52 1860 17 87 97 1864 12 97 112 1868 14 85 -93 1872 17 173 -173 1876 18 112 102 1880 20 66 72 1884 21 75 79 1888 22 80 80 1892 23 94 91 1896 24 56 52 1900 17 87 97 1904 12 97 112 1908 14 85 -93 1912 17 173 -173 1916 18 112 102 1920 20 66 72 1924 21 75 79 1928 22 80 80 1932 23 94 91 1936 24 56 52 1940 17 87 97 1944 12 97 112 1948 14 85 -93 1952 17 173 -173 1956 18 112 102 1960 20 66 72 1964 21 75 79 1968 22 80 80 1972 23 94 91 1976 24 56 52 1980 17 87 97 1984 12 97 112 1988 14 85 -93 1992 17 173 -173 1996 18 112 102 2000 20 66 72 2004 21 75 79 2008 22 80 80 2012 23 94 91 2016 24 56 52 2020 17 87 97 2024 12 97 112 2028 14 85 -93 2032 17 173 -173 2036 18 112 102 2040 20 66 72 2044 21 75 79 2048 22 80 80 2052 23 94 91 2056 24 56 52 2060 17 87 97 2064 12 97 112 2068 14 85 -93 2072 17 173 -173 2076 18 112 102 2080 20 66 72 2084 21 75 79 2088 22 80 80 2092 23 94 91 2096 24 56 52 2100 17 87 97 2104 12 97 112 2108 14 85 -93 2112 17 173 -173 2116 18 112 102 2120 20 66 72 2124 21 75 79 2128 22 80 80 2132 23 94 91 2136 24 56 52 2140 17 87 97 2144 12 97 112 2148 14 85 -93 2152 17 173 -173 2156 18 112 102 2160 20 66 72 2164 21 75 79 2168 22 80 80 2172 23 94 91 2176 24 56 52 2180 17 87 97 2184 12 97 112 2188 14 85 -93 2192 17 173 -173 2196 18 112 102 2200 20 66 72 2204 21 75 79 2208 22 80 80 2212 23 94 91 2216 24 56 52 2220 17 87 97 2224 12 97 112 2228 14 85 -93 2232 17 173 -173 2236 18 112 102 2240 20 66 72 2244 21 75 79 2248 22 80 80 2252 23 94 91 2256 24 56 52 2260 17 87 97 2264 12 97 112 2268 14 85 -93 2272 17 173 -173 2276 18 112 102 2280 20 66 72 2284 21 75 79 2288 22 80 80 2292 23 94 91 2296 24 56 52 2300 17 87 97 2304 12 97 112 2308 14 85 -93 2312 17 173 -173 2316 18 112 102 2320 20 66 72 2324 21 75 79 2328 22 80 80 2332 23 94 91 2336 24 56 52 2340 17 87 97 2344 12 97 112 2348 14 85 -93 2352 17 173 -173 2356 18 112 102 2360 20 66 72 2364 21 75 79 2368 22 80 80 2372 23 94 91 2376 24 56 52 2380 17 87 97 2384 12 97 112 2388 14 85 -93 2392 17 173 -173 2396 18 112 102 2400 20 66 72 2404 21 75 79 2408 22 80 80 2412 23 94 91 2416 24 56 52 2420 17 87 97 2424 12 97 112 2428 14 85 -93 2432 17 173 -173 2436 18 112 102 2440 20 66 72 2444 21 75 79 2448 22 80 80 2452 23 94 91 2456 24 56 52 2460 17 87 97 2464 12 97 112 2468 14 85 -93 2472 17 173 -173 2476 18 112 102 2480 20 66 72 2484 21 75 79 2488 22 80 80 2492 23 94 91 2496 24 56 52 2500 17 87 97 2504 12 97 112 2508 14 85 -93 2512 17 173 -173 2516 18 112 102 2520 20 66 72 2524 21 75 79 2528 22 80 80 2532 23 94 91 2536 24 56 52 2540 17 87 97 2544 12 97 112 2548 14 85 -93 2552 17 173 -173 2556 18 112 102 2560 20 66 72 2564 21 75 79 2568 22 80 80 2572 23 94 91 2576 24 56 52 2580 17 87 97 2584 12 97 112 2588 14 85 -93 2592 17 173 -173 2596 18 112 102 2600 20 66 72 2604 21 75 79 2608 22 80 80 2612 23 94 91 2616 24 56 52 2620 17 87 97 2624 12 97 112 2628 14 85 -93 2632 17 173 -173 2636 18 112 102 2640 20 66 72 2644 21 75 79 2648 22 80 80 2652 23 94 91 2656 24 56 52 2660 17 87 97 2664 12 97 112 2668 14 85 -93 2672 17 173 -173 2676 18 112 102 2680 20 66 72 2684 21 75 79 2688 22 80 80 2692 23 94 91 2696 24 56 52 2700 17 87 97 2704 12 97 112 2708 14 85 -93 2712 17 173 -173 2716 18 112 102 2720 20 66 72 2724 21 75 79 2728 22 80 80 2732 23 94 91 2736 24 56 52 2740 17 87 97 2744 12 97 112 2748 14 85 -93 2752 17 173 -173 2756 18 112 102 2760 20 66 72 2764 21 75 79 2768 22 80 80 2772 23 94 91 2776 24 56 52 2780 17 87 97 2784 12 97 112 2788 14 85 -93 2792 17 173 -173 2796 18 112 102 2800 20 66 72 2804 21 75 79 2808 22 80 80 2812 23 94 91 2816 24 56 52 2820 17 87 97 2824 12 97 112 2828 14 85 -93 2832 17 173 -173 2836 18 112 102 2840 20 66 72 2844 21 75 79 2848 22 80 80 2852 23 94 91 2856 24 56 52 2860 17 87 97 2864 12 97 112 2868 14 85 -93 2872 17 173 -173 2876 18 112 102 2880 20 66 72 2884 21 75 79 2888 22 80 80 2892 23 94 91 2896 24 56 52 2900 17 87 97 2904 12 97 112 2908 14 85 -93 2912 17 173 -173 2916 18 112 102 2920 20 66 72 2924 21 75 79 2928 22 80 80 2932 23 94 91 2936 24 56 52 2940 17 87 97 2944 12 97 112 2948 14 85 -93 2952 17 173 -173 2956 18 112 102 2960 20 66 72 2964 21 75 79 2968 22 80 80 2972 23 94 91 2976 24 56 52 2980 17 87 97 2984 12 97 112 2988 14 85 -93 2992 17 173 -173 2996 18 112 102 3000 20 66 72 3004 21 75 79 3008 22 80 80 3012 23 94 91 3016 24 56 52 3020 17 87 97 3024 12 97 112 3028 14 85 -93 3032 17 173 -173 3036 18 112 102 3040 20 66 72 3044 21 75 79 3048 22 80 80 3052 23 94 91 3056 24 56 52 3060 17 87 97 3064 12 97 112 3068 14 85 -93 3072 17 173 -173 3076 18 112 102 3080 20 66 72 3084 21 75 79 3088 22 80 80 3092 23 94 91 3096 24 56 52 3100 17 87 97 3104 12 97 112 3108 14 85 -93 3112 17 173 -173 3116 18 112 102 3120 20 66 72 3124 21 75 79 3128 22 80 80 3132 23 94 91 3136 24 56 52 3140 17 87 97 3144 12 97 112 3148 14 85 -93 3152 17 173 -173 3156 18 112 102 3160 20 66 72 3164 21 75 79 3168 22 80 80 3172 23 94 91 3176 24 56 52 3180 17 87 97 3184 12 97 112 3188 14 85 -93 3192</p>
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(given in parentheses) were derived from coordinates obtained by the method of Cruickshank (1961) following an analysis of the thermal motion of the molecules (Schomaker & Trueblood, 1968). The dimeric molecules were not expected to behave as rigid bodies, but the individual rings together with the atoms directly attached to them should do so to a good approximation. For the Cl-syndnone the root mean square difference between 'observed'  $U_{ij}$  and those calculated from the rigid body model was about 0.002 Å<sup>2</sup>, and for the H-syndnone the difference was 0.0014 Å<sup>2</sup>, indicating a quite good fit. The magnitudes of the principal axes of the translational and librational tensors are listed in Table 11. For H-syndnone and one of the Cl-syndnone

rings the maximum librational axis corresponds to a r.m.s. amplitude of about 10°, the direction in both cases being within ~20° of the direction of the N-C (ethylene) bond. The screw components were all small.

Table 11. *Principal components of rigid body translation and librational tensors*

Columns 1 and 2 contain r.m.s. translational amplitudes (Å) and r.m.s. librational amplitudes (degrees), respectively, for atoms O(1)–O(8) of Cl-syndnone, columns 3 and 4 contain those for O(11)–O(18), and columns 5 and 6 contain those for H-syndnone.

0.24	4.9	0.23	10.1	0.20	8.6
0.19	3.6	0.20	4.2	0.18	3.8
0.17	3.5	0.18	2.8	0.17	2.8

Table 9. *H-syndnone. Observed and calculated structure factors*

The columns are  $h, k, l, 10F_o, 10F_c$ , the phase angle (°) and  $100/(\sigma/F)$ .

4 0 0 1364 1340 180 200	13 1 1 227 231 277 361	5 1 3 1077 1065 272 238	1 1 5 344 332 133 419	11 1 7 183 180 134 323	14 2 10 83 85 56 349
8 0 0 1027 1036 0 238	15 1 1 294 304 196 311	7 1 3 693 693 237 293	3 1 5 437 436 179 374	13 1 7 210 190 241 310	16 2 2 10 86 106 456 436
12 0 0 153 132 180 361	17 1 1 259 257 118 317	9 1 3 683 672 173 278	5 1 5 408 401 256 309	15 1 7 304 300 122 310	2 2 1 10 195 184 164 372
16 0 0 198 197 12 317	19 1 2 108 107 12 317	11 1 3 579 579 172 300	7 1 7 89 88 369 361	17 7 8 89 86 369 361	6 4 10 192 192 45 323
20 0 0 203 198 0 374	21 1 1 20 8 130 168	13 1 3 265 269 21 327	9 1 5 647 639 131 270	19 1 7 742 747 130 257	4 10 10 129 131 174 327
4 2 0 702 712 180 330	2 2 2 1035 1046 304 275	15 1 3 490 485 172 300	11 1 3 415 415 172 300	13 1 3 310 310 164 321	8 10 10 103 100 208 353
8 2 0 217 217 111 310 508	6 0 2 2 1113 1113 0 320	17 1 3 84 82 199 285	13 1 5 259 268 118 317	4 0 8 746 755 352 251	12 10 94 92 206 408
6 2 0 451 442 180 374	10 0 2 1078 1078 103 215	19 1 3 166 168 6 365	15 1 5 405 415 351 285	8 0 8 123 121 225 302	14 10 91 91 23 181 508
8 2 0 1109 1113 192 320	12 0 2 2100 2100 310 210	21 3 3 21 177 177 317	12 0 2 210 210 43 365	12 0 8 371 377 139 290	10 10 47 46 255 268
10 2 0 688 683 0 268 10	18 0 2 276 275 18 323	0 0 4 349 340 251 455	19 1 5 106 111 182 397	16 0 8 262 267 66 361	8 10 39 29 272 238
12 2 0 530 540 0 263	22 0 2 80 92 15 523	4 2 2 990 908 67 236	2 0 6 23 229 3 436	6 2 8 623 618 57 257	6 10 34 10 203 85
14 2 0 16 6 75	2 2 2 2100 2102 65 104	8 0 4 990 908 67 236	4 0 6 1086 1052 0 215	2 8 2 157 143 333 365	4 10 10 103 103 208 353
16 2 0 17 2 180 71	4 2 2 2090 2081 132 125	12 0 4 990 908 67 236	10 0 6 261 266 50 337	6 2 8 278 286 216 311	10 10 47 46 255 268
18 2 0 158 153 0 317	6 2 2 271 275 250 462	16 0 4 465 476 27 359	14 0 6 183 190 321 316	12 2 8 277 286 216 311	8 10 39 29 272 238
20 2 0 40 71 180 320	8 2 2 604 601 303 303	20 0 4 93 92 51 452	18 0 6 135 143 120 378	14 2 8 278 286 216 311	6 10 39 29 272 238
0 4 0 547 547 160 317	10 2 2 256 257 18 402	2 2 2 298 297 339 436	0 2 6 517 506 120 329	16 2 8 277 286 216 311	4 10 39 29 272 238
2 4 0 486 504 0 334	12 2 2 388 385 12 334	4 2 4 285 289 112 369	6 2 8 281 276 256 368	18 2 8 89 91 88 361	8 10 39 29 272 238
4 4 0 202 207 0 402	14 2 2 269 268 352 334	6 2 4 704 680 325 283	8 2 6 257 251 282 387	10 2 8 89 91 88 361	6 10 39 29 272 238
6 4 0 547 547 160 317	16 2 2 338 338 228 302	8 2 4 284 286 170 363	10 2 6 172 173 162 369	12 2 8 89 91 88 361	4 10 39 29 272 238
8 4 0 317 327 180 334	18 2 2 41 31 228 200	10 2 4 260 264 250 327	12 2 6 336 341 21 314	14 2 8 89 91 88 361	2 10 86 65 256 428
10 4 0 62 55 0 253	2 4 2 440 451 196 337	12 2 4 101 104 190 314	14 2 6 398 400 191 288	16 2 8 246 237 199 305	10 10 39 29 272 238
12 4 0 290 288 180 305	4 4 2 347 356 350 353	16 2 4 186 195 79 361	18 2 6 256 258 231 306	2 10 86 65 256 428	8 10 39 29 272 238
14 4 0 411 405 180 296	6 4 2 604 609 278	20 2 4 88 83 221 94	20 2 6 52 48 341 248	14 2 8 118 121 95 367	6 10 39 29 272 238
16 4 0 85 85 180 302	8 4 2 399 407 250 311	0 4 4 1312 1335 104 185	2 6 6 104 100 265 357	10 2 8 180 182 155 366	4 10 39 29 272 238
18 4 0 22 19 160 126	10 4 2 158 159 353 334	2 4 4 543 548 224 299	4 6 4 206 207 21 337	12 2 8 224 214 266 383	2 10 86 65 256 428
4 6 0 0 191 186 0 330	12 4 2 298 303 88 308	4 4 4 665 688 242 266	6 4 6 328 327 145 320	10 6 4 42 44 13 314	10 10 39 29 272 238
6 6 0 380 380 180 290	14 4 2 162 157 164 327	6 4 4 188 191 256 361	8 4 6 306 307 21 337	2 6 8 169 167 138 334	8 10 39 29 272 238
8 6 0 111 114 190 311	16 4 2 95 99 117 317	8 4 4 339 339 116 314	10 4 6 476 482 196 270	6 8 6 28 25 291 128	6 10 39 29 272 238
10 6 0 180 186 180 320	18 4 2 89 92 88 387	10 4 4 65 81 325 251	12 4 6 78 78 280 362	8 6 8 73 78 213 305	4 10 39 29 272 238
12 6 0 166 163 0 361	0 6 2 258 247 327 317	12 4 4 89 91 110 293	14 4 6 55 59 114 231	10 6 8 125 120 273 419	2 10 86 65 256 428
14 6 0 56 66 180 269	2 6 2 172 169 317 330	14 4 6 89 91 110 293	16 4 6 81 89 350 357	12 6 8 101 93 232 498	10 10 39 29 272 238
16 6 0 65 64 0 402	4 6 2 171 175 158 327	16 4 6 215 216 300 357	18 4 6 116 119 191 401	14 6 8 300 299 299 498	8 10 39 29 272 238
0 8 0 94 78 0 217	6 6 2 178 184 142 323	18 4 6 235 237 235 317	2 6 6 619 673 194 234	2 8 8 109 109 209 498	6 10 39 29 272 238
2 8 0 117 111 180 345	8 6 2 133 134 127 314	2 6 6 235 237 235 317	4 6 6 231 346 261 297	4 6 6 76 76 124 265	4 10 39 29 272 238
4 8 0 21 3 0 160	10 6 2 190 186 308 327	4 6 6 215 216 300 357	6 6 6 285 280 15 305	6 6 6 285 280 15 305	2 10 86 65 256 428
6 8 0 68 64 180 320	12 6 2 228 232 154 336	6 6 6 215 216 300 357	8 6 6 104 100 265 357	10 6 6 15 23 116 78	10 10 39 29 272 238
8 8 0 204 194 0 347	14 6 2 90 84 147 357	8 6 6 170 164 253 323	12 6 6 66 66 298 334	14 6 6 15 23 116 78	8 10 39 29 272 238
10 8 0 169 180 400 408	16 6 2 150 147 249 483	10 6 6 188 185 93 361	14 6 6 104 100 265 357	16 6 6 15 23 116 78	6 10 39 29 272 238
1 9 1 35 36 257 263	2 8 2 48 37 47 239	12 6 6 4 43 30 189 285	16 6 6 15 23 116 78	18 6 6 15 23 116 78	4 10 39 29 272 238
3 9 1 94 93 360 462	4 8 2 155 146 75 365	14 6 6 4 43 30 189 285	18 6 6 66 66 298 334	2 8 6 66 66 298 334	2 10 86 65 256 428
5 9 1 12 12 144 362	6 8 2 112 112 142 362	16 6 6 4 43 30 189 285	2 8 6 156 148 8 413	4 8 6 156 148 8 413	2 10 86 65 256 428
7 9 1 101 94 175 317	8 8 2 83 80 152 378	18 6 6 4 43 30 189 285	4 8 6 21 23 6 160	6 8 6 21 23 6 160	2 10 86 65 256 428
9 9 1 177 175 45 330	10 8 2 123 113 0 462	2 8 6 483 480 363	6 8 6 53 47 280 365	8 8 6 53 47 280 365	2 10 86 65 256 428
11 9 1 132 126 306 327	12 8 2 111 105 269 476	4 8 6 183 171 55 283	8 8 6 76 80 3 483	10 8 6 76 80 3 483	2 10 86 65 256 428
13 9 1 35 36 257 263	14 8 2 78 73 173 455	6 8 6 103 100 336 406	12 8 6 76 80 3 483	14 8 6 76 80 3 483	2 10 86 65 256 428
15 9 1 94 93 360 462	16 8 2 89 87 147 462	8 8 6 80 77 258 624	14 8 6 76 80 3 483	16 8 6 76 80 3 483	2 10 86 65 256 428
17 9 1 101 94 175 317	18 8 2 65 61 249 476	10 8 6 59 54 2 476	16 8 6 76 80 3 483	18 8 6 76 80 3 483	2 10 86 65 256 428
19 9 1 132 126 306 327	2 9 2 104 111 298 317	12 8 6 59 54 2 476	18 8 6 76 80 3 483	2 9 2 104 111 298 317	2 10 86 65 256 428
1 10 1 155 156 334	4 9 2 104 111 298 317	14 8 6 59 54 2 476	2 9 2 104 111 298 317	4 9 2 104 111 298 317	2 10 86 65 256 428
3 10 1 23 11 241 147	6 9 2 104 111 298 317	16 8 6 59 54 2 476	4 9 2 104 111 298 317	6 9 2 104 111 298 317	2 10 86 65 256 428
5 10 1 144 144 53 442	8 9 2 104 111 298 317	18 8 6 59 54 2 476	6 9 2 104 111 298 317	8 9 2 104 111 298 317	2 10 86 65 256 428
7 10 1 187 177 319 378	10 9 2 104 111 298 317	2 9 2 104 111 298 317	8 9 2 104 111 298 317	10 9 2 104 111 298 317	2 10 86 65 256 428
9 10 1 271 280 46 349	12 9 2 104 111 298 317	4 9 2 104 111 298 317	10 9 2 104 111 298 317	12 9 2 104 111 298 317	2 10 86 65 256 428
11 10 1 115 109 231 361	14 9 2 104 111 298 317	6 9 2 104 111 298 317	12 9 2 104 111 298 317	14 9 2 104 111 298 317	2 10 86 65 256 428
13 10 1 44 62 183 320	16 9 2 104 111 298 317	8 9 2 104 111 298 317	14 9 2 104 111 298 317	16 9 2 104 111 298 317	2 10 86 65 256 428
15 10 1 429 435 303 285	18 9 2 104 111 298 317	10 9 2 104 111 298 317	16 9 2 104 111 298 317	18 9 2 104 111 298 317	2 10 86 65 256 428
17 10 1 287 284 25 310	2 10 2 104 111 298 317	12 9 2 104 111 298 317	18 9 2 104 111 298 317	2 10 2 104 111 298 317	2 10 86 65 256 428
19 10 1 218 218 0 330	4 10 2 104 111 298 317	14 9 2 104 111 298 317	2 10 2 104 111 298 317	4 10 2 104 111 298 317	2 10 86 65 256 428
1 11 1 177 175 45 330	6 10 2 104 111 298 317	16 9 2 104 111 298 317	4 10 2 104 111 298 317	6 10 2 104 111 298 317	2 10 86 65 256 428
3 11 1 410 410 0 320	8 10 2 104 111 298 317	18 9 2 104 111 298 317	6 10 2 104 111 298 317	8 10 2 104 111 298 317	2 10 86 65 256 428
5 11 1 126 126 306 327	10 10 2 104 111 298 317	2 10 2 104 111 298 317	8 10 2 104 111 298 317	10 10 2 104 111 298 317	2 10 86 65 256 428
7 11 1 84 77 230 299	12 10 2 104 111 298 317	4 10 2 104 111 298 317	10 10 2 104 111 298 317	12 10 2 104 111 298 317	2 10 86 65 256 428
9 11 1 136 135 104 334	14 10 2 104 111 298 317	6 10 2 104 111 298 317	12 10 2 104 111 298 317	14 10 2 104 111 298 317	2 10 86 65 256 428
11 11 1 23 11 241 147	16 10 2 104 111 298 317	8 10 2 104 111 298 317	14 10 2 104 111 298 317	16 10 2 104 111 298 317	2 10 86 65 256 428
13 11 1 144 144 53 442	18 10 2 104 111 298 317	10 10 2 104 111 298 317	16 10 2 104 111 298 317	18 10 2 104 111 298 317	2 10 86 65 256 428
15 11 1 187 177 319 378	2 11 2 104 111 298 317	12 10 2 104 111 298 317	18 10 2 104 111 298 317	2 11 2 104 111 298 317	2 10 86 65 256 428
17 11 1 271 280 46 349	4 11 2 104 111 298 317	14 10 2 104 111 298 317	2 11 2 104 111 298 317	4 11 2 104 111 298 317	2 10 86 65 256 428
19 11 1 115 109 231 361	6 11 2 104 111 298 317	16 10 2 104 111 298 317	4 11 2 104 111 298 317	6 11 2 104 111 298 317	2 10 86 65 256 428
1 12 1 44 62 183 320	8 11 2 104 111 298 317	18 10 2 104 111 298 317			

The equations of the least-squares planes defined by the two crystallographically independent rings of the Cl-sydnone and by the H-sydnone ring are given in Table 10, together with individual deviations of both cyclic and exocyclic atoms. The rings themselves are planar, the largest deviation being 0.007 Å, or about two standard deviations in the positional parameters, while most of the exocyclic atoms are displaced outward from the center of the molecule by ten to twenty standard deviations. The largest deviations (0.05–0.1 Å) are found in the methylene carbon atoms, indicating a slight bending of the N(3)–C(6) bond.

Comparative views of the two sydnones are shown in Fig. 6. While the H-sydnone is required to possess a twofold symmetry axis, no such restriction applies to the Cl-sydnone. Fig. 6(a) and (c) reflect the similarity in the torsion angles N(3)–C(6)–C(16)–N(13) in the two molecules: 73.4° for Cl-sydnone and 68.1° for H-sydnone. One of the rings in Cl-sydnone has essentially the same orientation with respect to the central C–C bond as that found in H-sydnone; the torsion angles

N(2)–N(3)–C(6)–C(16) are 66.1° and 73.1° respectively. However, as is clearly seen from Fig. 6(b), the other ring in Cl-sydnone is oriented differently, with the torsion angle N(12)–N(13)–C(16)–C(6) being only 14.3°. A torsion angle of about 60° makes one of the methylene C–H bonds coplanar with the ring, whereas a torsion angle of about 0° causes the central C–C bond and the ring to become coplanar.

The similarity found in the molecular geometry of three independent sydnone rings, together with the small estimated standard deviations, is sufficient to allow some general statements about this unusual ring system.

The rings are planar, and as pointed out in our previous communication (Thiessen & Hope, 1967) the ring O–N, N–N, N–C, and C–C distances are very close to corresponding bond distances found in other aromatic systems. However, the average ring C–O bond distance of 1.41 Å is very much longer than the C–O distance of 1.36 Å in furan (Bak, Christensen, Dixon, Hansen-Nygaard, Rastrup Andersen & Schott-

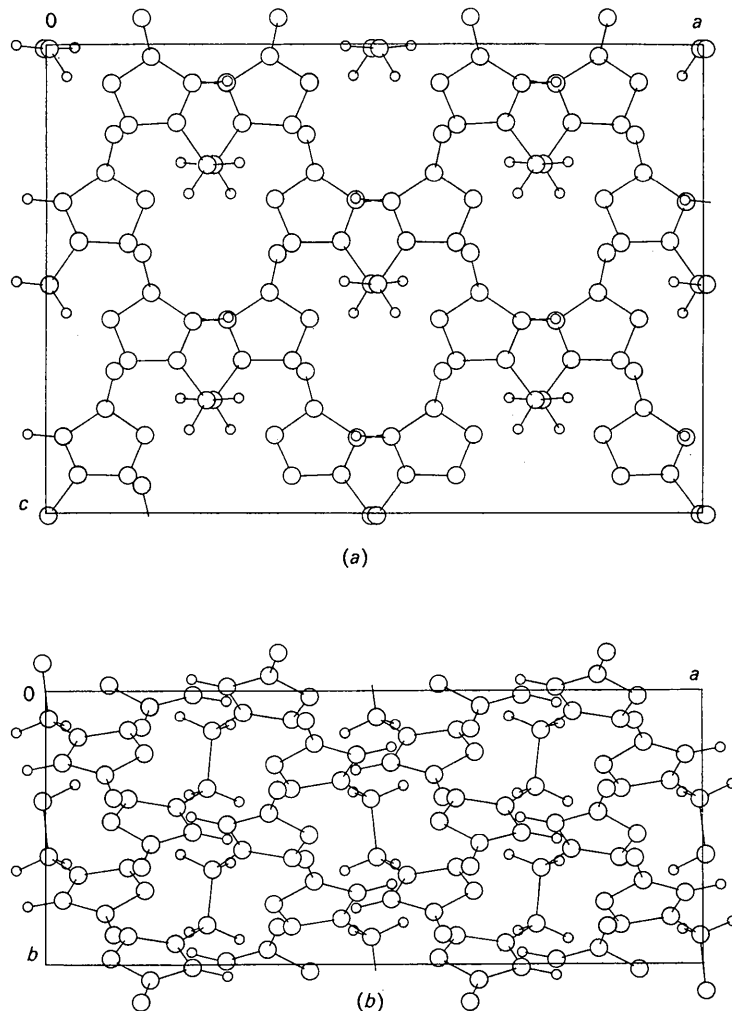


Fig. 3. (a) Projection of the structure of H-sydnone along the *b* axis. (b) Projection along the *c* axis.



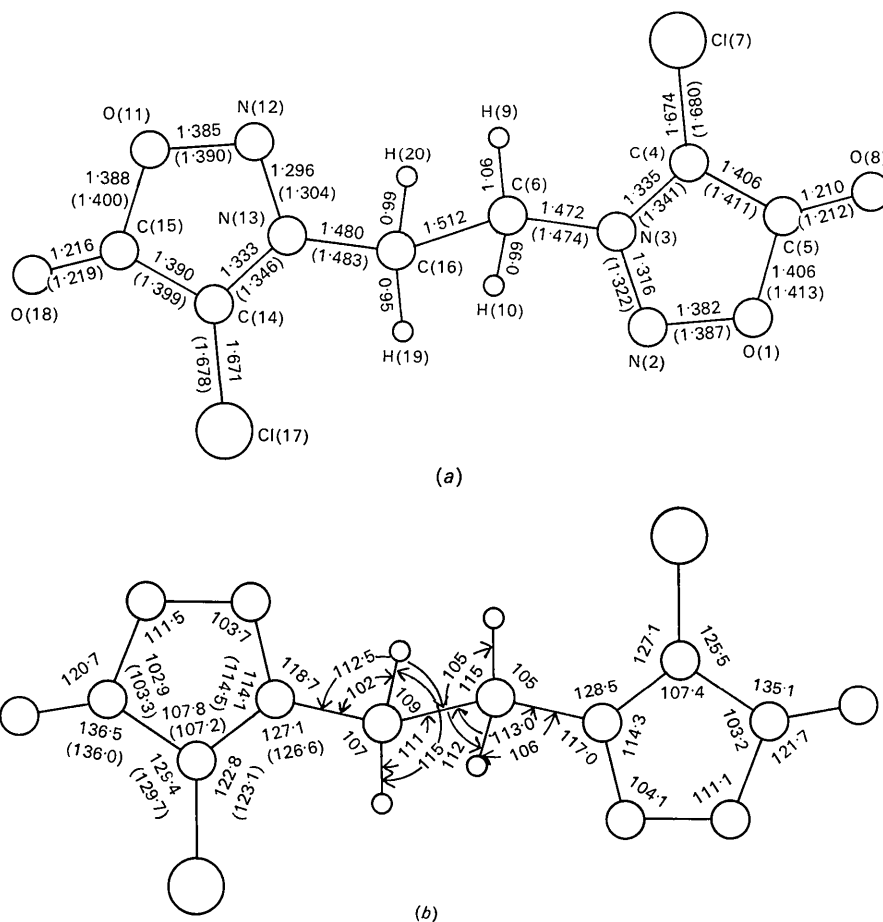


Fig. 4. (a) Interatomic distances in Cl-sydnone. Distances in parentheses have been corrected for anisotropic thermal motion effects. Estimated standard deviations are 0.004–0.006 Å for distances between C, N and O, 0.003 Å for C–Cl and 0.03–0.04 Å for C–H distances. (b) Bond angles. Angles in parentheses have been corrected for anisotropic thermal motion effects (given only if the correction exceeds  $1\sigma$ ). Estimated standard deviations are about  $0.3^\circ$  for angles not involving H, about  $2^\circ$  if one H is involved, and about  $3^\circ$  for two H atoms.

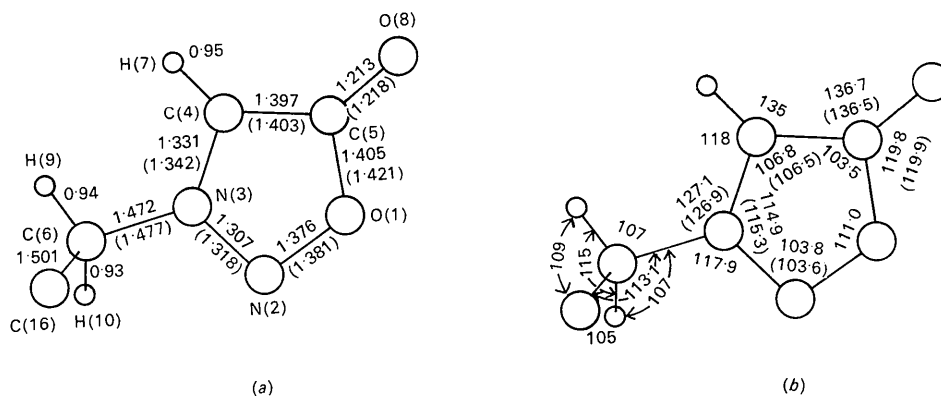
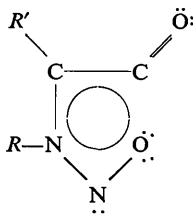


Fig. 5. (a) Interatomic distances in H-sydnone. Distances in parentheses have been corrected for anisotropic thermal motion effects. Estimated standard deviations are 0.002–0.003 Å for distances between C, N and O, and 0.02–0.03 Å for C–H. (b) Bond angles. Angles in parentheses have been corrected for anisotropic thermal motion effects (given only if the correction exceeds  $1\sigma$ ). Estimated standard deviations are  $0.1$ – $0.2^\circ$  for angles not involving H, and  $1$ – $2^\circ$  if H atoms are involved. Since the molecule possesses twofold symmetry, only the methylene carbon, C(16), is shown in addition to the half-molecule constituting the asymmetric unit.

länder, 1962). The exocyclic C=O distance (1.22 Å) lends no support to the formulation of Baker & Ollis (1957), which involves the delocalization of a positive charge on the ring, and a negative charge on the exocyclic oxygen.

In the Cl-sydnone, as we have already pointed out, the difference between the bond angles involving the exocyclic oxygen is unusually large. Since the same pattern is observed in the H-sydnone, we feel that this is an inherent property of the sydnone system rather than arising from the steric requirements of the chlorine atom.

In view of the experimental evidence that the sydnone ring is aromatic (Baker, Ollis & Poole, 1949) we find it useful to depart from the usual procedure of postulating a regular  $\sigma$  system and then feeding in the  $\pi$ -electrons. Instead we combine our observations of geometry with the assumed  $\pi$  system to postulate that an ordinary  $\sigma$  framework extends through the sequence O-N-N-C-C, whereas the  $\sigma$  component of the ring C-O bond has much less than normal weight. We suggest the formula



as the best single formula representation for the sydnone system.

We wish to emphasize that this representation of the carbonyl group is meant to indicate merely that the C=O bond is of normal double bond length; it may contain components of  $\pi$ -electron density both perpendicular to and in the plane of the ring.

Our observations do not yet permit us to answer the delicate question of the arrangement of the lone pair electrons on the exocyclic oxygen atom. In the hope of clarifying this point, we are investigating the structures of two types of compounds: molecular complexes with the carbonyl acting as donor group, and substances in which the acylimino (RCON=) moiety has been substituted for the carbonyl oxygen atom.

A literal interpretation of the suggested formula leads to a formal charge of +0.8 on N(3) and an equal negative charge distributed over the remaining ring atoms. We note with interest that this admittedly crude picture gives a calculated dipole moment of about 5 D, which is the same as that found experimentally for sydneses (Hill & Sutton, 1949).

The observed values of the two angles N-C-H (118°) and C-C-H (135°) in H-sydnone are such that even after allowance has been made for the standard deviations (2°) a sizable difference is indicated. A possible interpretation follows from the valence-shell electron-repulsion theory of Gillespie (1963). The electrons in the C-N bond will be displaced towards the relatively positive nitrogen and will repel the electron pair in the

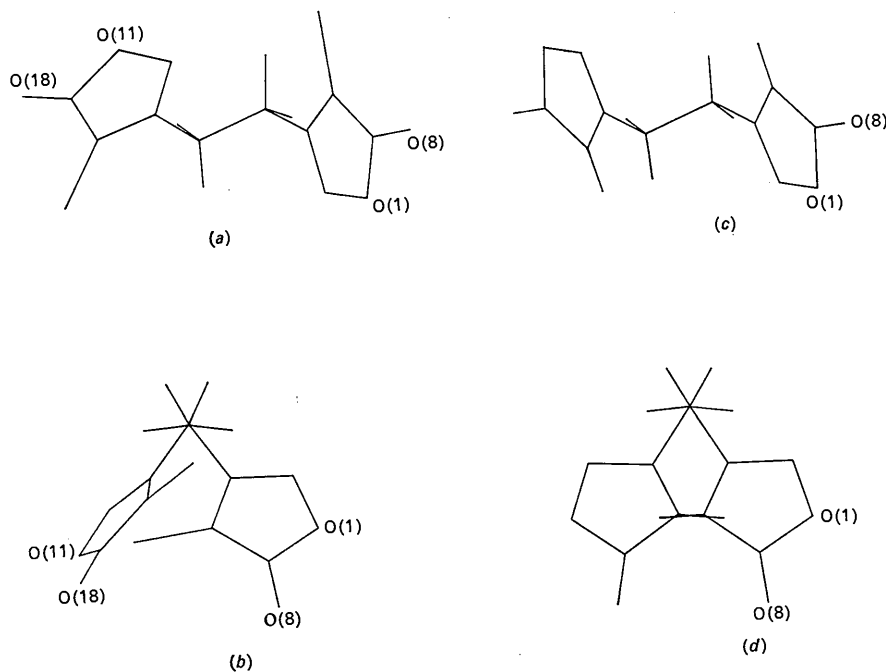


Fig. 6. (a) Cl-sydnone viewed along the vector defined by the midpoints of N(3)-N(13) and C(6)-C(16) respectively. (b) Cl-sydnone viewed along the central C-C bond. (c) H-sydnone viewed along the twofold axis. (d) H-sydnone viewed along the central C-C bond.

C-H bond to a lesser degree than will the more evenly distributed electrons in the C-C bond, causing the C-C-H angle to be larger than the N-C-H angle.

A similar effect would be expected in the Cl-sydnone, and the angles N(13)-C(14)-Cl(17) and C(15)-C(14)-Cl(17) actually show a difference of about 7°; however, the corresponding angles at C(4) do not differ appreciably. A possible explanation of this dissimilar behavior arises from the difference in orientation of the two rings with respect to the ethylene group as described above. Cl(7) is 'eclipsed' with respect to one of the methylene hydrogen atoms, H(9), while Cl(17) is in the 'staggered' configuration relative to its neighboring methylene group.

The angles associated with the nitrogen-methylene carbon bond differ from each other by amounts (8-11°) which are commonly encountered in planar groups where an exocyclic atom is flanked by another exocyclic atom on one side but not on the other.

The C-Cl distance in Cl-sydnone (1.68 Å) is 0.06 Å shorter than the normal C(aromatic)-Cl distance (Palenik, Donohue & Trueblood, 1968). The charge distribution implied in our proposed formula leads to a situation in which considerable delocalization of the chlorine lone-pair electrons onto the positive nitrogen is to be expected with consequent shortening of the C-Cl bond.

All intermolecular distances found in both structures are normal with the exception of one between O(18) and Cl(7) which is 2.98 Å, or about 0.2 Å less than the sum of van der Waals radii. This contact does not seem to have any appreciable effect on the geometry around the carbonyl carbon.

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## The Crystal Structure of Tetronic Acid Derivatives. II. $\alpha,\gamma$ -Dimethyltetronic Acid

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The structure of  $\alpha,\gamma$ -dimethyltetronic acid, C<sub>6</sub>H<sub>7</sub>O<sub>3</sub>, has been determined by obtaining the equation of the molecular plane by the method of Lawrence & MacDonald (*Acta Cryst.* (1968) **A24**, 579), and refined by least-squares techniques in three dimensions. The molecule is very similar in structure to that of  $\alpha$ -methyltetronic acid, and the resonance across the OH-C=C-CO chain and the strong hydrogen bonding found in the latter are again present.

### Introduction

Tetronic acid derivatives occur in a wide range of natural products, and their importance is discussed in a

previous paper (McDonald & Alleyne, 1963) in which the structure of  $\alpha$ -methyltetronic acid is described. The second member of the series to be investigated,  $\alpha,\gamma$ -dimethyltetronic acid (see Fig. 3) differs from the previous one only in the addition of a methyl group in the  $\gamma$  position. The molecule of  $\alpha$ -methyltetronic acid is planar, but it was believed that the carbon atom C(6)

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