are confined to the Cu sphere; the analysis by Cruickshank (1960) indicates that the accuracy with which thermal parameters are determined is improved by extending the intensity data to higher $(\sin\theta)/\lambda$ values, the data otherwise being of cqual quality.

We gratefully acknowledge the contributions of the following: Dr E. R. Ellers and the Carnegie Museum of Pittsburgh for supplying the geode from which the quartz crystals were obtained; the Computation and Data Processing Center of the University of Pittsburgh for providing computing facilities; Drs R. Shiono and P. Schapiro of the University of Pittsburgh for supplying some of the programs; Dr W. R. Busing for special programing assistance; Drs R. A. Young and B. Post for the opportunity to compare and discuss results in advance of publication; from Mellon Institute, Dr E. S. Hodge and Miss B. L. Ely of Research Services for the spectrographic analysis, Dr A. J. Cohen for the X-irradiation of the crystals and useful suggestions, and Miss P. E. Brown and Mr D. F. Hales for assistance with some of the calculations.

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The Structure of *N*-(*p*-bromophenyl)sydnone

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(*Received* 26 *July* 1962)

The crystal structure of *N*-(*p*-bromophenyl)sydnone has been determined. The compound crystallizes in space group $P\bar{1}$, with two molecules in the unit cell. The sydnone ring system is found to be planar within the limits of accuracy. The *N*-phenyl bond is (almost) coplanar with the sydnone ring, but the phenyl ring is rotated about this bond so that the planes of the phenyl ring and the sydnone ring contain a dihedral angle of 27·6°.

Introduction

Meso-ionic compounds, and in particular the sydnones, have received considerable interest in recent years. The chemical properties of meso-ionic compounds have been reviewed by Baker & Ollis (1957). Physicochemical studies of sydnones include investigations of dipole moments (Hill & Sutton, 1953), of ultraviolet spectra (Hammick & Voaden, 1961), and of polarographic behaviour (Zuman, 1959), and the determina-

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tion of unit-cell dimensions and space groups of a number of *N*-phenylsydnones (Schmidt, 1951). As detailed structural data of sydnones appeared not to have been reported, an investigation of the crystal structure of *N*-(*p*-bromophenyl)sydnone, the atomic skeleton of which is shown in Fig. 1, seemed worthwhile. The preliminary results of this investigation have been published elsewhere (Bärnighausen *et al.*, 1961); the full account of the structure determination is reported in this paper.

Experimental

A sample of *N*-(*p*-bromophenyl)sydnone was kindly provided by Prof. J. F. Arens. The compound is almost colourless; it crystallizes in needles along the *c* axis. The needles are nearly always twinned, the *c* axis being the twin axis. Therefore reflexions $hk0$ of one individual coincide with reflexions $\bar{h}\bar{k}0$ of the other; this is, however, not so for the reflexions of the higher layer lines around [001]. Nevertheless, on the second layer line non-equivalent reflexions of the two individuals nearly coincide. For the quantitative characterization of the twin the following terms were calculated (Donnay, 1959): twin index $n=2$, twin obliquity $\omega=1{\cdot}65°$. The plane of intergrowth lies in the zone [001], since the twin seams on the crystal faces are parallel to the needle axis, as could be seen under the microscope. From the relative positions of the two series of reflexions on the second layer line of a twinned crystal, we could determine the dimensions of the triclinic unit cell from rotation and Weissenberg diagrams around the *c* axis only. The following cell dimensions were found:

$$a=12{\cdot}31\pm0{\cdot}07,\ b=10{\cdot}17\pm0{\cdot}05,\ c=3{\cdot}92\pm0{\cdot}04\ \text{Å};$$
$$\alpha=79{\cdot}2\pm0{\cdot}1°,\ \beta=112{\cdot}7\pm0{\cdot}2°,\ \gamma=106{\cdot}3\pm0{\cdot}2°.$$

The corresponding reduced cell (Delaunay, 1933) has dimensions:

$$a'=11{\cdot}39,\ b'=10{\cdot}19,\ c'=3{\cdot}92\ \text{Å};$$
$$\alpha'=101{\cdot}4°,\ \beta'=94{\cdot}2°,\ \gamma'=102{\cdot}1°.$$

It is related to the cell used in this paper by:

$$\mathbf{a}'=\mathbf{a}+\mathbf{c},\ \mathbf{b}'=\mathbf{b}-\mathbf{c},\ \mathbf{c}'=\mathbf{c}\,.$$

For practical reasons (see below) the cell with the unprimed axes was preferred.* With two molecules of $C_8H_5N_2O_2Br$ per unit cell the density is calculated as 1·85 g.cm^{-3}.

For the intensity measurements untwinned crystals were found by laborious search among the material which was available. The cross-section of the individuals perpendicular to the *c* axis generally was a parallelogram with an angle of about 56° [angle between (100) and $(1\bar{1}0)$]; crystals with parallelogram edges of about 0·03 mm were selected. For such crystals μd for copper radiation is of the order of 0·1 and no absorption correction was considered necessary.

Integrated equi-inclination Weissenberg photographs (Wiebenga & Smits, 1950) of the zero, first, second and third layer lines about the *c* axis were taken with nickel-filtered copper radiation. The multiple-film technique was applied. The reflexion intensities were measured with a densitometer of the type described by Smits & Wiebenga (1953). The crystals proved to be sensitive to light and to X-rays; they became brown during exposure. Although it was found that this decomposition did not significantly affect the reflexion intensities, a new crystal was used for every layer line.† Attempts to obtain good Weissenberg diagrams about other rotation axes failed. Therefore the scale factors for the individual layer lines were calculated by statistical methods, making plausible assumptions about the thermal movement in the *c* direction (see below). The scale factors derived in this way were consistent with rough experimental scale factors determined from precession diagrams (Mo $K\alpha$ radiation) about the *a'* and *b* axes.

Determination of the structure

In contradistinction to the intensities reported for the asymmetric crystals of L-tyrosine HBr (Peterson, 1955), the intensities of pairs of reflexions hkl and $\bar{h}\bar{k}\bar{l}$ from *N*-(*p*-bromophenyl)sydnone did not show significant differences due to the anomalous scattering of Cu $K\alpha$ radiation by the Br atoms. The crystals were therefore assumed to be centrosymmetric, space group $P\bar{1}$. Approximate atomic parameters were derived from Patterson projections along the *b* and *c* axes and refined by Fourier projections along the same axes. In the structure-factor calculations atomic scattering factors of C, N and O were taken from Berghuis *et al.* (1955); the Br scattering factors from Thomas & Umeda (1957) were adopted with corrections for the real part—but not for the imaginary part—of the anomalous scattering (Dauben & Templeton, 1955).

A three-dimensional electron-density map was computed (Bärnighausen *et al.*, 1961). The setting of the unit cell was chosen in such a way that the *z* parameters of the atoms of one molecule cover a small range only; thus, a relatively small number of electron-density sections (with constant *z*) was sufficient. Refinement proceeded by successive cycles of structure-factor calculations and three-dimensional difference syntheses (Cochran, 1951).

A complete refinement of the thermal parameters

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* In the preliminary note (Bärnighausen *et al.*, 1961) still another setting is given with axes corresponding to *a'*, *b* and *c*.

† The $hk0$ reflexion intensities of one particular crystal corresponded to a much larger overall temperature factor than was found for all other crystals, although the atomic positions and the anisotropy of the thermal movement deduced from these intensities did not show significant deviations. The cause of this effect is not evident.

was not attempted. We confined ourselves to the isotropic refinement of the C, N and O atoms, but the strong anisotropy in the thermal movement of Br had to be taken into account. In the planes parallel to (001) the minimum of thermal vibration was found in the direction of the Br–C$_1$ bond which is almost parallel to the a axis. The magnitude of the vibration perpendicular to (001) could not be precisely determined from our experimental data, because of the rather inaccurate experimental scaling of the various layer lines. Therefore, we assumed the thermal movement of Br to be the same in all directions perpendicular to the Br–C$_1$ bond, or rather perpendicular to a. The anisotropy of the Br temperature vibration was included in the structure-factor computations by substituting the Br atom by nine 'fractional atoms' (Vos & Smits, 1961). The scaling of the layer lines deduced by equalizing ΣF_o and ΣF_c for each layer line, was consistent with the experimental one.

After three cycles of three-dimensional refinement the value of R of the 954 independent reflexions was 8·2% and the atomic shifts were considerably less than the standard deviation of the positional parameters. An estimate of this standard deviation was obtained from the r.m.s. slopes in the difference maps at positions far from atomic sites. The r.m.s. errors in the final parameters were found as 0·01 Å for C, N and O and as 0·001 Å for Br; these standard deviations do not take account of the errors in the cell dimensions. The estimated errors in the final parameters correspond to a standard deviation of 0·01 Å in the C–Br distance, and to a standard deviation of 0·014 Å in the bond lengths and of 0·9° in the bond angles involving C, N and O atoms. The latter estimates can be compared with the values of 0·022 Å and 0·84° respectively, calculated from the deviations of the phenyl ring from a regular hexagon.

The final positional and thermal parameters of Br, C, N and O are listed in Table 1. Table 1 also contains the hydrogen positions calculated with a C–H distance of 1·08 Å. These positions correspond to regions of high electron density in a final difference synthesis which was calculated for reflexions with $\sin\theta < 0{\cdot}5$ only (Jellinek, 1958). However, a few spurious peaks of almost equal height were also present in this synthesis, especially in the neighbourhood of the Br atom. In the final structure-factor calculation (Table 2) the hydrogen atoms were introduced in the calculated positions with scattering factors as calculated by McWeeny (1951), and an isotropic temperature parameter B of 3·8 Å^2, which is equal to the average of the values found for the C, N and O atoms. The final value of the disagreement index R is 8·2% for the observed reflexions.

All calculations were carried out by the digital computer ZEBRA with programs devised by Dr D. W. Smits.

Results

The observed bond distances and angles in the N-(p-bromophenyl)sydnone molecule are shown in Fig. 1. It is seen that the C–C bonds in the phenyl ring (observed average length: 1·393 ± 0·009 Å) have their usual lengths. In the sydnone ring system the distances N$_2$–O$_1$ and C$_8$–O$_1$ are not significantly different from single-bond distances, while the length of the C$_8$–O$_2$ bond corresponds to that of a double bond. The N$_1$–N$_2$, N$_1$–C$_7$ and C$_7$–C$_8$ bond distances, however, are intermediate between those of single and double bonds.

For both the phenyl ring and the sydnone ring we calculated the best least squares plane with a program devised by Dr D. Rogers; the observed distances of the atoms from these planes are included in Table 1. The two rings appear to be planar within

Table 1. *Final positional and thermal parameters*

	x	y	z	B	Distance from phenyl plane	Distance from sydnone plane
Br	−0·07036	0·24541	0·6795	3·01 (∥ a) Å^2 5·36 (⊥ a)	−0·004 Å	−0·077 Å
C$_1$	0·0864	0·2502	0·6990	3·9	−0·009	−0·075
C$_2$	0·1651	0·3723	0·6490	4·5	+0·005	−0·605
C$_3$	0·2792	0·3742	0·6636	3·8	+0·000	−0·598
C$_4$	0·3151	0·2496	0·7348	3·0	−0·003	−0·027
C$_5$	0·2356	0·1245	0·7910	3·7	−0·000	+0·532
C$_6$	0·1227	0·1235	0·7765	4·0	+0·006	+0·523
C$_7$	0·4636	0·1401	0·6725	3·4	−0·528	+0·012
C$_8$	0·5870	0·1905	0·7181	3·1	−0·329	−0·011
N$_1$	0·4305	0·2469	0·7493	3·2	−0·018	−0·008
N$_2$	0·5203	0·3581	0·8502	4·7	+0·521	+0·001
O$_1$	0·6181	0·3246	0·8345	4·0	+0·344	+0·007
O$_2$	0·6635	0·1465	0·6880	4·6	−0·567	−0·018
H$_2$	0·1369	0·4679	0·5976			
H$_3$	0·3390	0·4709	0·6203			
H$_5$	0·2617	0·0274	0·8462			
H$_6$	0·0643	0·0261	0·8245			
H$_7$	0·4062	0·0404	0·5948			

Table 2. *Observed and calculated structure factors for the observed reflexions*

h	F_o	F_c
	h,0,0	
1	12.0	12.4
2	42.3	40.1
3	12.2	11.7
4	24.0	24.2-
5	36.2	33.7-
6	35.8	35.3-
7	28.7	27.8-
8	23.4	24.7-
9	12.9	12.1-
12	8.1	8.2
13	9.4	8.8
	h,1,0	
-12	11.8	11.9
-11	10.3	9.7
-10	17.4	17.4
- 9	22.1	21.5
- 8	8.1	8.2
- 6	45.3	42.1-
- 5	20.6	21.5-
- 4	50.8	49.8-
- 3	55.8	56.4-
- 2	12.9	12.3-
0	9.0	9.7
2	13.5	14.1
3	62.4	60.0
4	42.3	41.7
5	16.3	17.2
6	29.6	27.0
8	10.9	9.6-
10	19.3	19.1-
11	11.2	13.0-
12	7.7	6.9-
	h,2,0	
-14	6.2	6.4-
-13	8.8	9.4-
-12	10.9	12.5-
-11	7.3	5.9
-10	5.1	2.2
- 9	22.1	22.6
- 8	22.3	22.3
- 7	21.9	22.6
- 6	37.3	36.9
- 5	40.3	37.7
- 3	8.6	8.7-
- 2	45.9	45.5-
- 1	36.0	34.5-
0	107.9	106.9-
1	22.7	21.5-
2	48.7	44.6-
3	31.1	23.4-
4	34.3	33.7
5	10.5	11.0
6	33.0	33.8
7	28.1	28.7
8	29.8	31.6
11	6.9	5.9-
13	6.2	6.3-
	h,3,0	
-12	12.9	13.1-
-11	9.7	8.9-
-10	15.7	16.7-
- 9	21.4	20.3-
- 6	24.2	23.3
- 5	33.7	34.6
- 4	36.9	36.5
- 3	30.0	29.5
- 2	51.5	51.4
- 1	27.0	23.5
0	9.0	8.3-
1	31.3	29.6-
2	45.9	45.6-
3	31.1	32.0-
4	22.9	23.1-
5	18.0	19.8-
6	11.2	10.1-
10	15.2	15.5
11	7.7	9.3
	h,4,0	
-14	6.4	7.3
-13	9.2	8.5
-12	9.0	9.3
- 9	16.9	17.6-
- 8	32.4	32.4-
- 7	22.9	23.5-
- 6	39.2	38.8-
- 5	13.9	13.3-
- 4	7.9	7.6-
- 3	22.3	23.7
- 2	41.4	41.7
- 1	46.5	48.7
0	15.2	17.9
1	41.0	39.2
2	26.8	26.1
3	19.9	16.0
4	17.6	16.5-
5	12.7	14.5-
6	25.7	26.0-
7	13.9	16.5-
8	21.7	21.8-
	h,5,0	
-12	11.4	12.1
-11	12.4	11.9
-10	19.3	10.5
- 6	13.3	13.5-
- 5	30.2	30.5-
- 4	18.9	20.3-
- 3	16.3	15.9-
- 2	44.8	44.2-
1	7.1	7.4
2	44.6	44.0
3	8.6	12.3
4	18.9	19.1
5	14.2	16.9
10	6.0	8.6-
	h,6,0	
-13	6.2	7.1-
- 8	30.0	30.7
- 7	19.1	9.3
- 6	27.2	27.2
- 5	7.7	7.9
- 4	9.7	7.0
- 3	16.3	15.8-
- 2	21.4	23.2-
- 1	32.2	33.7-
0	19.3	21.7-
1	31.1	30.9-
5	17.8	20.5
6	12.9	13.3
8	6.9	8.7
	h,7,0	
-12	8.6	8.3-
-11	9.2	10.3-
-10	14.8	15.2-
- 6	14.2	15.2
- 5	13.3	14.2
- 4	19.5	21.2
- 3	13.5	14.1
- 2	17.6	18.2
- 1	10.3	9.9-
0	4.7	3.3-
1	8.4	4.5
2	22.5	22.5-
4	13.7	14.6-
5	9.0	8.3-
9	7.5	6.1
	h,8,0	
-10	8.8	9.8-
- 8	14.8	15.5-
- 7	11.8	12.2-
- 6	9.9	10.2-
- 5	10.3	12.2-
- 3	5.1	6.2
- 2	7.1	9.2
- 1	12.9	15.7
0	27.9	29.3
1	10.3	12.5
3	7.5	5.0-
5	15.0	15.0-
	h,9,0	
-11	6.4	5.3
-10	6.0	8.0
- 8	8.6	7.0
- 7	7.3	7.2-
- 6	12.2	13.3-
- 4	15.7	16.9-
- 2	5.1	7.5-
- 1	7.5	5.7
2	9.0	10.6
	h,10,0	
-10	6.6	6.2
- 5	8.8	10.9
0	14.2	13.0-
	h,11,0	
- 4	4.5	7.8
	h,12,0	
- 2	6.0	5.8
	h,-10,1	
- 2	7.9	6.9-
2	8.6	8.1
4	8.1	8.2
	h,-9,1	
- 5	9.6	7.7
- 2	6.5	7.0-
- 1	6.5	7.4-
0	20.8	15.9-
1	6.5	7.3-
5	11.0	11.0
6	6.0	7.1
	h,-8,1	
- 5	6.2	7.8
- 4	11.3	11.4
- 2	15.3	11.8
- 1	13.7	7.2-
0	6.7	5.0-
1	9.3	3.9
2	12.7	12.4-
3	9.3	9.5-
4	13.7	11.7-
6	6.5	6.9-
8	7.2	8.0
9	9.3	3.7
	h,-7,1	
- 8	5.7	8.2-
- 6	6.5	6.7-
- 5	14.8	13.3-
- 4	9.3	5.7
- 1	24.4	22.6
0	23.2	22.5
1	19.9	19.5
4	9.1	11.6-
5	11.5	10.0-
6	18.2	18.1-
7	9.3	7.1-
8	14.6	11.2-
	h,-6,1	
- 9	4.1	4.7
- 8	6.2	4.7
- 7	8.1	7.8-
- 6	10.5	10.6-
- 5	13.0	16.7-
- 4	18.7	17.4-
- 3	12.7	9.2-
- 2	22.0	19.9-
- 1	12.9	11.6
0	12.7	9.5
2	28.3	27.2
3	13.2	15.4
4	12.0	11.8
5	11.0	11.1
6	4.6	4.2
7	9.3	8.0-
8	6.5	3.9-
10	11.7	11.4-
11	4.8	5.8-
12	3.6	5.2-
	h,-5,1	
-10	8.1	8.4
- 9	6.5	7.1
- 8	14.8	15.2
- 7	6.7	8.2
- 6	18.9	17.4
- 5	6.2	6.7
- 3	17.5	15.2-
- 2	18.7	17.8-
- 1	33.5	33.8-
0	18.0	19.0-
1	24.2	25.6-
2	15.6	14.0-
3	5.5	4.3-
4	14.4	13.7
5	15.1	13.8
6	24.4	25.2
7	14.6	15.3
8	16.2	19.6
9	6.5	6.1
10	10.5	8.5-
12	9.6	6.3-
	h,-4,1	
-11	5.7	7.1-
-10	11.0	13.1-
- 7	6.5	6.7
- 6	18.9	18.0
- 5	22.8	23.5
- 4	19.4	19.8
- 3	18.2	19.3
- 2	23.2	22.7
- 1	6.5	4.7
0	8.6	8.6-
1	29.5	27.0-
2	44.1	44.2-
3	21.3	19.8-
4	17.7	15.3-
5	14.1	14.5-
7	14.4	15.6
9	9.3	8.4
10	12.9	11.6
11	5.5	5.7
12	7.9	6.2
	h,-3,1	
-10	6.5	8.5-
- 9	6.7	5.8-
- 8	28.5	29.5-
- 7	22.3	23.7-
- 6	23.9	25.2-
- 4	16.5	16.0-
- 3	38.6	37.0
- 2	53.6	52.3
- 1	21.1	20.8
0	44.5	45.9
1	11.5	11.6
2	26.3	26.5
4	14.6	14.0-
5	27.5	26.1-
6	25.4	25.0-
7	21.1	19.8-
8	16.5	15.2-
9	9.3	9.3-
10	9.1	6.7
12	10.3	9.4
13	8.9	7.0
	h,-2,1	
-14	5.7	6.1
-13	4.8	6.7
-12	10.1	11.6
-11	13.4	14.9
-10	21.1	18.7
- 9	9.1	7.1-
- 8	6.2	5.1-
- 7	7.9	5.0-
- 6	31.4	30.5-
- 5	25.6	25.3-
- 4	30.4	30.5-
- 3	33.5	34.7-
- 2	11.7	4.4-
- 1	12.7	13.0-
0	10.5	8.9
1	45.7	48.0
2	32.1	32.1
3	32.8	33.9
4	29.0	28.8
5	5.3	6.1
6	12.7	12.0
7	10.8	10.6-
8	9.3	9.6-
9	19.6	16.9-
10	16.0	12.3-
12	4.8	5.1-
	h,-1,1	
-10	6.7	5.9
- 9	14.1	17.7
- 8	33.8	34.8
- 7	37.4	33.8
- 6	24.2	23.7
- 5	6.7	6.4
- 4	10.5	7.6
- 3	35.4	34.4-
- 2	63.7	65.9-
- 1	6.0	1.3-
0	112.6	130.8-
2	18.4	19.1-
3	5.7	4.2
4	25.9	26.1
5	35.4	34.0
6	27.5	29.1
7	15.3	16.4
8	13.4	10.2
12	9.6	8.7-
	h,0,1	
-14	7.7	7.9-
-13	5.7	7.5-
-12	17.5	16.7-
-11	14.8	15.7-
-10	14.6	16.4-
- 9	8.6	7.9-
- 8	9.6	8.0
- 7	11.3	9.8
- 6	49.6	48.9
- 5	29.7	30.3
- 4	48.1	50.2
- 3	41.2	44.0
- 2	2.6	1.9-
- 1	29.9	31.3-
0	29.7	31.8-
1	17.7	19.3-
2	13.2	12.0-
3	42.2	45.9-
4	25.4	26.3-
6	16.3	15.6-
7	6.2	6.3
8	16.3	16.0
9	13.7	11.6
10	14.4	13.4
11	5.5	5.9
	h,1,1	
-15	5.7	8.2
-14	5.0	6.5
-13	7.2	7.3
-12	6.5	8.1
-11	12.9	13.7-
-10	9.1	8.6-
- 9	29.9	29.5-
- 8	29.9	29.1-
- 7	17.2	19.0-
- 6	25.4	26.5-
- 5	29.2	27.2-
- 4	13.4	14.2
- 3	19.6	19.9
- 2	34.5	37.1
- 1	28.0	31.0
0	109.9	131.2
1	20.4	20.3
2	10.5	5.8
4	35.7	36.8-
5	22.0	21.4-
6	29.2	30.5-
7	18.7	15.5-
8	16.5	16.2-
11	5.3	6.8
	h,2,1	
-14	4.6	6.8
-13	7.4	10.6
-12	18.0	18.9
-11	10.5	10.6
-10	10.1	13.2
- 9	23.0	20.9
- 8	12.2	10.2-
- 7	15.3	14.0-
- 6	51.5	51.0-
- 5	45.5	47.1-
- 4	40.5	42.5-
- 3	30.9	31.4-
- 2	19.6	19.4-
- 1	30.7	30.6
0	33.8	33.2
1	20.8	21.7
2	35.2	36.4
3	32.3	33.6
4	17.5	13.6
5	3.8	6.1
7	13.4	10.9-
8	13.7	12.2-
10	13.4	11.4-
11	6.9	7.0-
	h,3,1	
-15	6.9	8.8-
-14	6.5	8.0-
-13	5.3	7.0-
-12	5.7	8.3-
-11	12.9	14.0
-10	9.6	11.0
- 9	31.4	31.2
- 8	34.0	32.8
- 7	11.0	11.7
- 6	35.9	36.0
- 5	6.2	5.7
- 4	11.3	12.2-
- 3	30.9	32.0-
- 2	40.0	40.7-
- 1	54.6	57.4-
0	25.6	25.1-
1	27.3	26.5-
2	9.6	15.1-
3	4.8	2.2-
4	24.7	24.4
5	14.6	15.9
6	23.5	23.3
7	11.5	13.6
8	19.6	18.9
	h,4,1	
-14	4.6	7.1-
-13	9.6	12.2-
-12	19.4	17.9-
-11	8.9	10.7-
-10	17.7	17.6-
- 9	5.3	4.3-
- 8	12.7	13.1
- 7	11.5	12.5
- 6	28.0	28.5
- 5	45.3	44.7
- 4	26.8	26.7
- 3	10.5	8.5
- 2	34.5	35.1
- 1	6.2	7.9-
0	18.4	19.9-
1	22.3	21.6-
2	51.7	53.4-
3	11.0	11.7-
4	13.2	11.0-
5	8.9	9.4-
6	6.5	5.9
7	11.5	8.5
8	9.1	8.1
	h,5,1	
-15	3.1	6.5
-14	4.2	7.9
-13	4.1	5.9
-11	4.8	5.6-
-10	10.3	11.6-
- 9	12.2	13.4-
- 8	37.4	33.5-
- 7	18.4	21.2-
- 6	29.2	27.8-
- 5	4.1	3.6
- 3	33.1	33.4
- 2	40.5	41.1
- 1	39.8	41.3
0	4.1	6.8
1	22.5	21.0
2	4.8	6.3
3	7.7	7.6-
4	5.3	6.5-
5	19.2	20.8-
6	10.5	13.1-
	h,6,1	
-14	8.9	8.7
-13	8.4	10.0
-12	12.2	14.1
-11	14.8	14.6
-10	19.6	19.2
- 9	14.4	12.7-
- 8	9.3	8.7-
- 7	13.2	13.2-
- 6	23.5	23.9-
- 5	25.4	25.7-
- 4	20.1	21.6-
- 3	5.7	5.0-
- 2	19.9	17.6-
- 1	12.9	10.9
0	16.0	14.1
1	8.4	9.7
2	31.4	32.7
4	9.8	10.1
	h,7,1	
-14	4.8	5.9-
-10	10.5	13.0
- 8	26.1	26.3
- 7	22.0	19.8
- 6	6.7	7.3
- 3	21.3	18.9-
- 2	20.4	21.3-
- 1	18.4	18.1-
0	24.2	24.5-
1	6.2	9.4-
3	12.0	11.1
4	6.7	1.5
5	14.6	17.6
	h,8,1	
-14	5.5	6.8-
-13	5.3	8.8-
-12	5.9	8.5-
-11	12.0	10.7-
-10	10.3	11.0-
- 7	12.7	13.7
- 6	20.4	21.4
- 5	7.2	10.2
- 4	22.3	22.1
- 1	14.4	13.8-
0	12.5	12.3-
2	10.5	12.6-
	h,9,1	
-10	11.7	12.8-
- 9	7.2	9.2-
- 8	10.3	11.1-
- 7	12.9	10.2-
- 5	10.5	9.1-
- 4	10.5	9.0
- 3	7.4	8.5
- 2	7.4	8.2
0	24.7	21.9
	h,10,1	
- 6	12.7	14.0-
- 4	10.3	12.1-
- 1	7.2	6.1
0	7.2	7.9
	h,-8,2	
0	8.7	9.8-
	h,-7,2	
- 1	14.3	13.4-
0	11.9	11.1-
	h,-6,2	
- 3	10.2	10.1
- 1	16.4	16.5
0	15.1	13.5
1	10.0	11.2
4	6.2	9.6-
6	10.4	12.4-
	h,-5,2	
- 7	13.0	10.4-
- 6	17.3	16.3-
- 5	15.1	16.2-
- 4	13.6	11.1-
- 3	10.9	9.2-
- 1	15.1	12.6
0	11.7	12.5
1	13.4	12.2
2	19.2	19.7
3	10.0	9.9
7	8.5	11.7-
	h,-4,2	
-10	10.2	12.7
- 8	18.1	15.5
- 6	12.8	10.9
- 3	21.7	22.2-
- 2	28.1	26.3-
- 1	14.9	12.3-
0	21.1	19.6-
4	11.9	11.5
5	14.7	13.8
6	7.2	10.6
	h,-3,2	
-10	8.9	10.5-
- 8	12.1	8.5
- 7	11.5	10.9
- 6	25.6	25.4
- 5	21.5	19.1
- 4	14.3	13.5
- 3	6.8	11.0
0	11.7	10.2-
1	32.6	33.8-
2	24.5	23.2-
3	15.3	13.7-
4	7.7	7.6-
7	9.4	13.8
	h,-2,2	
-11	6.6	8.0-
- 8	25.8	24.4-
- 7	21.1	19.6-
- 6	10.0	8.7-
- 3	31.1	30.3
- 2	49.2	49.9
0	39.0	41.2
1	10.9	11.9-
3	6.0	5.8-
4	16.6	17.2-
5	19.4	17.5-
6	14.3	12.4-
7	7.2	8.2-
	h,-1,2	
-14	8.7	10.0
-13	6.8	8.1
-12	13.6	14.2
-11	13.2	14.0
-10	10.2	10.5
- 8	21.9	21.7-
- 7	16.0	12.8-
- 6	35.2	33.9-
- 5	22.8	22.0-
- 4	25.4	24.6-
- 3	9.6	11.0-
- 2	6.2	5.9
- 1	13.6	11.3
0	21.1	20.9
1	29.0	32.4
2	16.6	14.9
3	19.4	19.6
4	9.8	10.0
8	7.9	10.3-
	h,0,2	
-11	17.5	18.0
- 9	18.3	18.9
- 8	24.5	26.3
- 7	16.8	15.7
- 6	7.7	6.6
- 4	20.7	19.9-
- 3	25.8	25.3-
- 2	33.5	35.9-
- 1	10.9	9.5-
0	50.3	58.3-
2	5.8	6.5
3	8.9	7.1
4	24.3	24.2
5	18.5	16.5
6	19.4	18.3
	h,1,2	
-14	9.6	10.5-
-13	10.0	11.0-
-12	17.9	17.4-
-11	11.7	10.7-
- 8	23.7	21.9
- 7	20.5	18.6
- 6	41.6	41.9
- 5	32.8	34.8
- 4	24.7	26.5
- 3	10.7	13.0
- 1	34.3	40.2-
0	33.0	36.6-
1	13.0	13.0-
2	17.3	16.5-
3	17.9	18.0-
	h,2,2	
-11	21.3	20.1-
-10	14.9	14.3-
- 9	30.0	29.5-
- 8	25.1	24.5-
- 6	14.1	13.7-
- 4	21.7	23.1
- 3	24.7	26.3
- 2	16.4	15.3
- 1	29.6	32.0
0	31.1	29.4
1	14.9	14.3
2	7.9	8.4-
3	8.7	8.9-
4	20.5	19.9-
5	11.5	12.3-
6	17.5	15.6-
	h,3,2	
-14	8.5	10.3
-13	16.0	14.6
-12	16.0	17.5
- 8	17.3	15.1-
- 7	24.3	23.2-
- 6	37.5	36.5-
- 5	38.4	38.9-
- 4	18.8	19.2-
- 2	7.7	8.5-
- 1	29.8	29.5
0	30.0	28.6
1	13.9	12.4
2	30.3	32.7
	h,4,2	
-11	13.4	12.4
-10	22.2	23.1
- 9	19.6	19.7
- 8	26.9	24.3
- 6	15.3	14.3
- 5	15.1	14.6-
- 4	13.6	14.6-
- 3	30.9	30.0-
- 2	28.1	28.1-
- 1	30.7	31.1-
1	6.0	6.1-
3	7.2	10.3
4	7.7	8.0
5	13.2	13.9
	h,5,2	
-14	12.1	11.5-
-13	14.9	14.0-
-12	17.0	14.7-
-11	7.9	7.1-
-10	15.3	12.9-
- 9	17.7	16.0
- 8	16.2	14.7
- 7	21.7	21.4
- 6	25.8	26.1
- 5	24.9	24.3
- 4	16.4	14.8
- 3	6.8	6.1-
- 1	13.6	12.8-
0	17.3	16.8-
1	15.3	13.8-
2	28.3	29.5-
	h,6,2	
-10	18.3	17.5-
- 9	6.6	4.6-
- 8	22.6	23.7-
- 7	16.4	15.9-
- 4	10.0	9.6
- 3	24.3	24.2
- 2	26.0	26.0
- 1	16.4	14.3
5	14.1	13.2-
	h,7,2	
-14	8.3	10.5
-13	9.2	11.3
-12	9.2	9.7
-11	9.8	11.2
-10	10.0	10.8
- 9	18.5	18.0-
- 8	10.7	11.3-
- 7	18.1	17.6-
- 6	21.7	22.5-
- 5	9.2	10.0-
- 4	15.3	16.1-
- 1	12.6	12.1
0	13.6	13.6
2	11.1	12.9
	h,8,2	
- 8	12.4	12.4
- 7	11.9	11.4
- 4	8.9	11.6-
- 3	12.1	12.7-
- 2	9.8	10.7-
0	15.6	15.9-
	h,9,2	
- 7	10.2	11.9
- 6	17.0	16.9
- 4	9.6	11.5
	h,-8,3	
- 1	2.9	5.6
	h,-7,3	
0	3.4	4.7-
	h,-6,3	
- 8	2.9	0.9
- 7	4.9	6.6
- 6	7.3	8.3
- 5	6.9	7.6
- 1	11.4	11.9-
0	7.4	8.8-
2	3.6	5.1-
	h,-5,3	
-10	8.5	8.4-
- 9	3.1	4.6-
- 8	3.4	5.9-
- 7	3.8	2.8
- 5	6.0	6.4
- 4	4.0	3.4
- 3	9.6	9.5
- 2	6.0	6.2
0	8.9	8.8
2	3.8	2.8-
4	3.4	5.2-
5	4.2	5.3-
	h,-4,3	
- 9	3.6	5.1-
- 8	3.8	4.0-
- 7	8.3	8.0-
- 6	15.2	14.7-
- 5	8.9	8.8-
- 2	3.8	4.5
- 1	10.7	9.9
0	6.5	7.0
1	12.5	13.2
2	10.2	8.1
7	6.0	8.3-
	h,-3,3	
-11	4.4	6.1
-10	7.6	9.0
- 9	5.4	5.5
- 8	10.9	9.3
- 5	9.3	9.2-
- 4	5.8	4.6-
- 3	14.5	13.8-
- 2	20.0	21.2-
0	12.0	12.3-
1	8.3	10.2
3	3.4	3.1
4	5.1	7.6
5	4.9	6.5
	h,-2,3	
-13	5.4	5.7-
-12	8.0	7.7-
-11	4.0	4.8-
- 9	9.1	7.7
- 8	16.2	16.7
- 7	10.3	9.3
- 6	18.5	18.6
- 5	12.7	[illegible]
- 4	6.4	5.9
- 3	3.3	2.9-
- 2	7.1	7.6-
- 1	9.6	6.6-
0	10.2	8.3-
1	15.6	18.7-
2	11.8	9.0-
3	3.4	4.9-
5	3.3	5.7
7	4.7	[illegible]
	h,-1,3	
-13	2.5	2.5-
-12	3.1	3.8-

the limits of accuracy; the planes of the rings do not coincide, however, but contain a dihedral angle of 27·6°. This twisting of the molecule is probably to be ascribed to the repulsion of H_5 and H_7.

The co-ordination of N_1 is found to be planar; the plane through N_1 and its three neighbours does not quite coincide with the mean plane of the atoms of the sydnone ring, but the difference is barely significant. The observed angle contained by the N_1–C_4 bond and the plane of the sydnone ring is 0·8°. The (near-) coplanarity of the N_1–C_4 bond with the sydnone ring is in agreement with studies of the dipole moments of sydnones by Hill & Sutton (1953).

Two intermolecular approaches in *N*-(*p*-bromophenyl)sydnone deserve some discussion. The atom O_2 of one molecule approaches Br′ of another molecule

Table 2 (*cont.*)

h	F_o	F_o	h	F_o	F_c	h	F_o	F_o	h	F_o	F_o	h	F_o	F_c	h	F_o	F_c	h	F_o	F_c	h	F_o	F_c
−11	14.2	15.0−	−8	23.1	24.0−	−2	8.7	7.0−	6	2.9	4.6	−12	11.6	10.1	−4	11.1	9.6−	2	8.5	9.9−	−9	12.7	12.0−
−9	5.6	5.8−	−7	14.9	12.8−	−1	9.3	8.6−				−9	13.8	13.8−	−3	17.1	16.1−				−8	10.9	10.7−
−8	14.0	13.0−	−6	20.7	19.8−	0	13.6	11.7−		h,3,3		−8	11.8	9.5−	−2	13.8	14.0−		h,7,3		−7	10.3	10.3−
−7	6.7	6.1−	−5	15.2	15.2−	2	7.6	9.1				−7	17.2	18.0−	−1	6.0	6.8−				−6	12.9	12.5−
−6	4.0	3.6	−4	9.1	7.9−	3	6.4	7.1	−13	2.5	4.1−	−6	20.1	20.5−	1	6.0	6.3	−13	3.6	3.7−	−4	6.0	6.0−
−5	9.6	7.8	−3	5.3	3.6	4	10.0	10.1	−12	7.3	5.4−	−5	14.3	13.6−	3	6.0	7.4	−12	10.2	9.8−	−3	7.4	6.3
−4	12.5	11.3	−2	8.0	6.7	5	6.0	6.1	−11	13.6	12.8−	−4	6.9	5.8−	5	4.4	6.6	−11	9.4	8.3−	−1	10.0	8.1
−3	16.2	15.6	−1	15.8	16.9	6	6.4	8.2	−10	16.7	16.9−	−3	8.0	6.7				−10	11.3	10.1−	0	8.5	8.3
−2	21.4	23.8	0	16.9	18.9				−9	14.9	14.6−	−2	3.8	2.5		h,6,3		−8	6.0	6.8−			
−1	3.1	0.1	1	10.5	9.8		h,2,3		−8	12.7	12.2−	−1	16.0	16.0				−7	7.1	7.4−		h,9,3	
0	13.1	14.4	2	10.3	7.4				−7	10.0	11.0	0	15.2	14.4	−14	10.2	9.8−	−6	12.0	10.7			
1	6.9	9.0−	3	7.1	5.1	−15	5.1	6.9−	−5	13.1	13.6	1	6.7	5.7	−13	10.5	10.1−	−5	4.0	3.1	−12	4.9	5.3
2	4.4	5.2−	5	5.1	6.5−	−14	10.2	9.6−	−4	13.8	14.5	2	14.5	15.1	−12	6.0	6.5−	−4	9.8	8.2	−11	7.3	8.2
3	4.4	4.1−				−13	11.6	10.1−	−3	17.8	17.6	6	4.0	6.0−	−11	4.0	2.6−	−3	10.9	10.6	−10	3.1	6.1
4	10.0	11.2−		h,1,3		−12	11.4	10.9−	−2	7.8	4.7				−9	18.3	18.6	−2	11.8	10.7	−6	6.9	7.2−
5	5.4	6.0−				−9	7.3	5.8	−1	12.0	11.8		h,5,3		−8	13.2	12.5	0	5.6	4.7	−4	8.3	7.6−
6	6.0	6.2−	−13	3.1	3.8	−8	15.8	15.6	2	5.6	4.0−				−7	15.6	15.0	1	6.4	5.5−	−3	4.2	5.6−
			−12	4.7	4.2	−7	16.5	17.4	3	8.0	8.9−	−15	3.3	2.6−	−6	16.0	16.4	3	3.1	4.2−	0	4.5	5.5−
	h,0,3		−11	18.5	18.8	−6	20.9	22.5	4	4.4	4.6−	−13	4.0	3.9	−5	6.0	4.6						
			−10	7.4	6.3	−5	17.1	20.3	5	5.1	6.8−	−12	10.9	9.0	−4	7.8	7.1		h,8,3			h,10,3	
−14	9.8	9.3	−9	12.5	12.7	−4	6.0	6.0				−11	10.0	7.3	−3	12.2	11.3−						
−13	8.2	7.0	−8	13.8	13.2	−2	6.2	2.9−		h,4,3		−10	17.1	18.3	−2	4.4	3.9−	−14	5.4	6.8	−8	4.2	5.1
−12	10.7	9.7	−7	3.8	4.1−	−1	22.3	26.8−				−9	6.2	5.4	−1	10.2	7.9−	−13	7.4	5.0	−7	2.4	6.1
−11	8.5	7.4	−5	9.6	9.8−	0	21.4	23.6−	−15	6.7	6.4	−8	11.4	10.5	0	10.0	8.3−	−12	3.6	3.3	−6	6.7	7.5
−10	3.4	0.9	−4	14.2	17.1−	1	4.0	2.1−	−14	10.3	10.3	−6	5.8	6.0−	1	5.6	6.5−	−11	3.1	4.6	−1	6.5	7.2−
−9	7.1	6.1−	−3	14.0	16.6−	2	11.8	11.3−	−13	12.0	11.6	−5	12.7	10.6−									

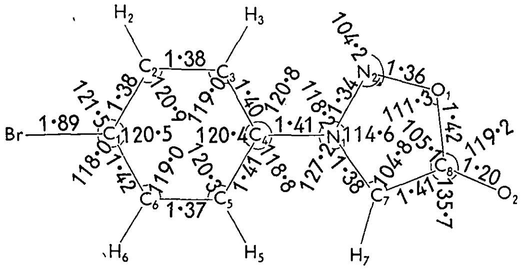

Fig. 1. Observed bond distances (in Å) and angles (in degrees) in the *N*-(*p*-bromophenyl)sydnone molecule. The planes of the phenyl ring and of the sydnone ring contain an angle of 27·6°.

(related to the first by translation along the *a* axis) at a distance of 3·16 Å, about 0·2 Å less than the sum of the van der Waals radii. This intermolecular contact is probably to be ascribed to a charge-transfer interaction,* as in oxalyl bromide (Groth & Hassel, 1961). The slight elongation of the Br–phenyl bond in comparison with the normal value of 1·85 Å, and the remarkable distortion of the bond angles around C_8 may also be ascribed to this interaction. The weak $O_2 \cdots Br'$ bonds link the molecules to chains parallel to the *a* axis. Furthermore, there is a short intermolecular contact of 3·20 Å between the atom O_2 of the molecule under consideration and the atom C_7'' of the centrosymmetrically related molecule. Intermolecular $O \cdots C$ approaches of a similar length have been observed in a number of compounds (Sime & Abrahams, 1960), but in the sydnone the bond C_7''–H_7'' points almost directly in the direction of O_2 and the calculated distance $O_2 \cdots H_7''$ is 2·2 Å which again is less than the sum of the van der Waals radii. There is thus an intermolecular interaction between these atoms, so that the molecules seem to be weakly linked to 'dimers' across a center. The other intermolecular contacts are not significantly shorter than the corresponding sums of the van der Waals radii.

We wish to thank Prof. E. H. Wiebenga for his interest throughout the course of this investigation, and Dr D. W. Smits, Mr D. Zaagman, Mr H. Schurer and Mr E. F. van Polen for their assistance. A stipend awarded to one of us (H. B.) from the funds of Prof. Theo Goldschmidt is gratefully acknowledged.

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* *Note added in proof*: A change-transfer complex of *N*-phenylsydnone and iodine has been described by Yamada & Kozima (1960).