N atom {[*N*-methyl and 3-(*p*-chlorophenyl)]-3,4-dihydro-1*H*-2,3-benzothiazine 2,2-dioxide, 1.634 (6) and 1.641 (4) Å, respectively (Rivero, Bianchet & Bravo, 1991*b*, 1993)}. The S—N length is considerably shorter than the normal single-bond value of 1.67–1.68 Å, which indicates electron delocalization within the SN group. A search of the July 1991 edition of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed that no other 2,3-benzothiazine structures have been reported. However, 1,2-benzothiazines are relatively common (Kojić-Prodić & Ružić-Toroš, 1982; Norris, Berke & Lombardino, 1985; Golič & Leban, 1987).

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Structure of 4-Methylpyridinium Bromide

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Abstract. γ-Picolinium bromide, [C₆H₇NH]Br, M_r = 174.05, monoclinic, *Cm*, a = 8.785 (4), b = 8.318 (3), c = 4.920 (1) Å, β = 103.62 (3)°, V = 349.4 (4) Å³, Z = 2, D_x = 1.654 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 57.23 cm⁻¹, $F(000)$ = 172, T = 293 K, R = 0.033 for 415 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 41 variables. The compound consists of C₆H₇NH⁺ cations and Br⁻ anions. Both species reside on crystallographic mirror planes defined by the Br, N(1), C(4), C(7) and H(71) atoms. The Br—N distance is 3.12 (1) Å.

Experimental. The title compound was prepared in the following manner. Under argon, a solution of

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* This work was performed while the author held a National Research Council–NASA Research Associateship.

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copper(I) bromide dimethyl sulfide [CuBr·S(CH$_3$)$_2$] (0.62 g, 3 mmol) and tetraethylthiuram disulfide [(C$_2$H$_5$)$_2$NCS$_2$]$_2$ (0.89 g, 3 mmol) in 25 ml of 4-methylpyridine was stirred for three days at 293 K. Filtration and layering of the 4-methylpyridine solution with 30 ml of hexane afforded colorless crystals of the title compound. A crystal of dimensions 0.52 × 0.31 × 0.22 mm was sealed inside a glass capillary. Cell constants were determined from least-squares refinement of 22 reflections having $18 < \theta < 22°$, using an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected with the ω–2θ scan technique in the range $4 < 2\theta < 55°$. The scan rate varied from 2 to 16° min^{-1} with ω-scan width = (0.96 + 0.350tanθ)°. Intensities were corrected for Lorentz and polarization effects, and for absorption effects based on the empirical method of Walker & Stuart (1983); relative $T_{min} = 0.446$, $T_{max} = 1.000$. Within the index ranges, $0 \le h \le 11$, $0 \le k \le 10$, $-6 \le l \le 6$, 430 unique reflections were collected of which 415 are classified as observed, $F_o^2 > 3\sigma(F_o)^2$. The structure was solved using the Patterson function which revealed the position of the Br atom. The remaining non-H atoms were located and refined, with anisotropic temperature factors, by a series of difference Fourier maps and least-squares refinements on F. The function minimized was $w(|F_o| - |F_c|)^2$ and the weight, w, defined by the Killean & Lawrence (1969) method with terms of 0.020 and 0.1. The H atoms were located from a difference Fourier map and added to the structure-factor calculations, but their positions were not refined. The final refinement parameters are: $R = 0.033$, $wR = 0.043$, $S = 1.540$ and $(\Delta/\sigma)_{max} = 0.00$. The maximum residual peak in the final difference Fourier map was 0.52 e Å^{-3}. Both absolute structures were refined under identical conditions, and the structure leading to the lower residual values is reported here. The final refinement parameters for the other absolute structure are: $R = 0.035$, $wR = 0.043$ and $S = 1.570$. Atomic scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). Plots of $w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using Enraf–Nonius MolEN (Enraf–Nonius, 1990). Final positional parameters and equivalent isotropic thermal parameters are listed in Table 1.* Bond

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

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Br	0.9	1	−0.2	3.68 (1)
N(1)	0.626 (1)	1	0.106 (2)	3.5 (2)
C(2)	0.5724 (9)	0.8595 (9)	0.178 (2)	4.0 (1)
C(3)	0.4635 (8)	0.8566 (9)	0.329 (2)	3.9 (1)
C(4)	0.402 (1)	1	0.412 (2)	3.3 (2)
C(7)	0.278 (2)	1	0.572 (3)	5.2 (3)
H(21)	0.613	0.763	0.121	5.1†
H(31)	0.427	0.756	0.382	5.0†
H(71)	0.32 (3)	1.000	0.76 (4)	7 (6)†
H(72)	0.213	0.907	0.520	6.8†

† H atoms were included in the structure-factor calculations but were not refined; $B(H) = 1.3 \times B(C)$.

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Br—N(1)	3.12 (1)	C(3)—C(4)	1.41 (1)
N(1)—C(2)	1.34 (1)	C(4)—C(7)	1.49 (2)
C(2)—C(3)	1.34 (1)		

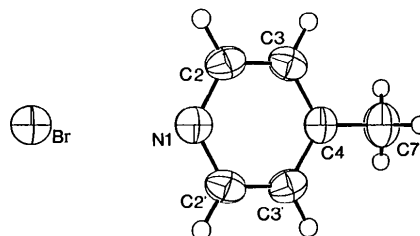| Br—N(1)—C(2)	119.2 (5)	C(2)—C(3)—C(4)	121.1 (7)
Br—N(1)—C(2')	119.2 (5)	C(3)—C(4)—C(3')	115.8 (9)
C(2)—N(1)—C(2')	121.4 (9)	C(3)—C(4)—C(7)	122.1 (5)
N(1)—C(2)·C(3)	120.4 (7)		

Fig. 1. *ORTEP* (Johnson, 1965) drawing depicting the stereochemistry of the [C$_6$H$_7$NH]Br molecule and the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Isotropic H-atom thermal parameters are represented by spheres of arbitrary size.

distances and angles are listed in Table 2. The stereochemistry of the molecule is illustrated in the *ORTEP* (Johnson, 1965) drawing in Fig. 1.

Related literature. ^{1}H NMR spectrum, viscosity and conductance measurements of 4-methylpyridinium bromide (Newman, Tillack, Morgan & Wan, 1977). X-ray structural characterization of piperidinium chloride (Gaudet, Zaworotko & White, 1989).

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Structure of Diphenyl Carbonate

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Abstract. Phenyl phenoxyformate, $C_{13}H_{10}O_3$, $M_r = 214.2$, orthorhombic, $P2_12_12_1$, $a = 6.062$ (2), $b = 7.242$ (1), $c = 23.375$ (4) Å, $V = 1026.2$ Å^3, $Z = 4$, $D_x = 1.387$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.92$ cm^{-1}, $F(000) = 448$, $T = 164$ K, $R = 0.0384$ for 1375 unique reflections with $I > 2\sigma(I)$. Diphenyl carbonate constitutes the simplest congener in the aromatic polycarbonate family. The two O—C$_{carbonyl}$ bond lengths are 1.345 (2) and 1.337 (2) Å. The O—C bond length of the carbonyl moiety is 1.191 (3) Å. The two C$_{aryl}$—O—C$_{carbonyl}$ angles are 118.4 (2) and 118.8 (2)°, while the two O—C$_{carbonyl}$—O$_{carbonyl}$ angles are 127.5 (2) and 127.8 (2)°. The two benzene rings are canted relative to the plane defined by the carbonate group. The dihedral angles between each benezene ring and the carbonate plane are 52.7 (2) and 57.7 (2)°.

Experimental. Compound (1), obtained by reaction of phosgene with phenol and triethylamine in methylene chloride, recrystallized from anhydrous ethanol at 298 K. A crystal was sealed in a glass

(1)
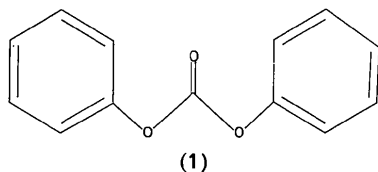
capillary for low-temperature data collection on a Siemens *R3m/V* upgrade of a Nicolet *P3F* automated diffractometer, using Wyckoff scans of variable scan speed. The structure was solved by direct methods and refined on *F* using the *SHELXTL-Plus* (Micro-

Table 1. *Experimental details*

Crystal	
Habit	Hexagonal rod
Size (mm)	0.52 × 0.24 × 0.24
Lattice-parameters determination	
No. of reflections	22
2θ range (°)	14.8–26.7
Reflection range	
h	−7 to 7
k	−9 to 2
l	−7 to 30
Maximum $\sin\theta/\lambda$ (Å^{-1})	0.650
Check reflections	$0\bar{1}\bar{6}$, $1\bar{1}\bar{3}$
Variation (%)	6, 5
Reflections	
Collected	1495
Unique observed	1375
R_{int}	0.0161
Observed criterion	$I > 2\sigma(I)$
No. of parameters	146
R	0.0384
wR	0.0418
S	1.75
Secondary-extinction parameters, χ, in $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	0.0032 (5)
Weighting factor, g, in $w^{-1} = \sigma^2(F) + gF^2$	0.0002
Difference Fourier peaks	
Minimum (e Å^{-3})	−0.20
Maximum (e Å^{-3})	0.28
Maximum (Δ/σ)	0.005

VAX II) program package (Sheldrick, 1988). H atoms were placed in idealized positions and constrained to have C—H = 0.96 Å and isotropic thermal parameters, $U = 0.08$ Å^2. All non-H atoms were treated as anisotropic. No absorption correction was applied. A correction for secondary extinction of the type described by Zachariasen (1967) refined in the later stages with a maximum correction of 25% for the 041 reflection. There were no apparent groups of