(1976), $\Delta C_2^s = 14\cdot 5$ $(1\cdot 0)°$ and $\Delta C_s^0 = 10\cdot 0$ $(1\cdot 0)°$, indicate that the conformation of the ring is twisted and between 'half-chair' (C_2) and 'envelope' (C_s). Finally, C(8) is $-0\cdot 14$ (1) Å out of the plane of C(5)—C(6)—S(1) on the same side as the methyl and the quaternary group.

The crystal packing, as viewed down **a**, is depicted in Fig. 3 and it is mainly determined by Coulombic and van der Waals forces. The intermolecular non-bonding distances are as expected for standard van der Waals values. The environment of the I^- anions is approximately tetrahedral with $I^-\cdots N^+$ distances ranging from 4·3 to 5·0 Å.

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Tetramethylammonium Benzotriazolide, $C_4H_{12}N^+.C_6H_4N_3^-$

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Abstract. $M_r = 192\cdot 27$, orthorhombic, $P2_12_12_1$, $a = 8\cdot 342$ (2), $b = 10\cdot 797$ (2), $c = 12\cdot 265$ (7) Å, $Z = 4$, $V = 1104\cdot 7$ (7) Å³, $D_x = 1\cdot 156$ Mg m⁻³, $\lambda(Cu\,K\alpha) = 1\cdot 5418$ Å, $\mu(Cu\,K\alpha) = 0\cdot 590$ mm⁻¹, final $R = 0\cdot 050$ for 941 reflections. The benzotriazolide ion is planar and has approximate *mm* symmetry.

Introduction. Benzotriazole is receiving increasing interest because of the biological activity of some of its derivatives on the one hand (Sparatore, La Rotonda, Paglietti, Ramundo, Silipo & Vittoria, 1978), and because of its use as a corrosion inhibitor for Cu and Cu alloys on the other (Søtofte & Nielsen, 1981a,b,c; Himes, Mighell & Siedle, 1981).

In order to gain a better knowledge of this heterocycle we have carried out X-ray investigations of crystal structures containing the benzotriazol-1-yl and -2-yl residues and the benzotriazolium cation (Giordano & Zagari, 1977, 1978; Giordano 1980). Here the structure of the benzotriazolide anion is presented.

Experimental. Deliquescent elongated prisms obtained by evaporation over P_2O_5 of an equimolar solution of

benzotriazole and tetramethylammonium hydroxide, $0\cdot 2 \times 0\cdot 3 \times 0\cdot 2$ mm, Lindemann capillary tube, Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$, three monitoring reflections, 1349 independent with $\theta < 75°$, 941 with $I > 3\sigma(I)$, Lp correction, absorption ignored; direct methods (*MULTAN* 78; Main, Lessinger, Woolfson, Germain & Declercq, 1978), anisotropic full matrix, H (from ΔF synthesis) isotropic, final $R = 0\cdot 050$, $R_w = 0\cdot 064$, $w = 1/\sigma^2$ (F_o),* secondary-extinction value $G = 4\cdot 6(0\cdot 7) \times 10^{-6}$, $F(000) = 416$, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), PDP 11/34 computer, Enraf–Nonius SDP software.

Discussion. The final atomic parameters are listed in Table 1. The dimensions of the benzotriazolide and tetramethylammonium ions are shown in Fig. 1, together with the atomic numbering scheme. The benzotriazolide anion has approximate *mm* symmetry.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38145 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and isotropic thermal parameters* ($\times 10$) *with e.s.d.'s in parentheses*

Equivalent B's defined as $(B_{11} \times B_{22} \times B_{33})^{1/3}$ are given for non-hydrogen atoms.

	x	y	z	$B_{eq}/B_{iso}(\text{Å}^2)$
N(1)	421 (4)	318 (3)	4187 (2)	66 (1)
N(2)	−603 (4)	−544 (2)	4538 (2)	70 (1)
N(3)	−1074 (4)	−363 (2)	5565 (3)	65 (1)
N(4)	4478 (3)	−1059 (2)	6154 (2)	48 (1)
C(4)	−387 (4)	1341 (4)	6878 (3)	65 (2)
C(5)	494 (5)	2400 (4)	6946 (3)	72 (2)
C(6)	1428 (5)	2819 (3)	6077 (3)	67 (2)
C(7)	1504 (4)	2200 (3)	5120 (3)	62 (2)
C(8)	596 (4)	1120 (3)	5030 (3)	50 (1)
C(9)	−328 (4)	695 (3)	5889 (3)	49 (1)
C(10)	5723 (4)	−1813 (3)	6695 (3)	59 (2)
C(11)	2902 (4)	−1509 (4)	6520 (3)	71 (2)
C(12)	4648 (5)	−1184 (4)	4960 (3)	70 (2)
C(13)	4690 (5)	270 (3)	6479 (3)	63 (2)
H(4)	−102 (4)	113 (4)	736 (3)	79 (9)
H(5)	39 (4)	292 (3)	756 (3)	78 (9)
H(6)	253 (4)	350 (4)	619 (3)	79 (9)
H(7)	219 (3)	241 (2)	461 (2)	39 (6)
H(101)	688 (6)	−141 (5)	643 (4)	124 (15)
H(102)	577 (3)	−168 (2)	750 (2)	39 (6)
H(103)	555 (5)	−270 (4)	649 (3)	91 (11)
H(111)	289 (3)	−130 (3)	719 (2)	47 (6)
H(112)	265 (5)	−238 (4)	633 (3)	114 (14)
H(113)	207 (4)	−110 (4)	602 (3)	76 (9)
H(121)	585 (4)	−80 (3)	473 (3)	64 (9)
H(122)	383 (4)	−69 (3)	455 (3)	77 (10)
H(123)	455 (5)	−196 (3)	477 (3)	95 (12)
H(131)	482 (5)	36 (4)	732 (4)	110 (12)
H(132)	392 (4)	69 (3)	617 (3)	65 (9)
H(133)	576 (4)	53 (3)	613 (3)	65 (8)

Fig. 2. Bond orders and resonance forms with their percentage contributions.
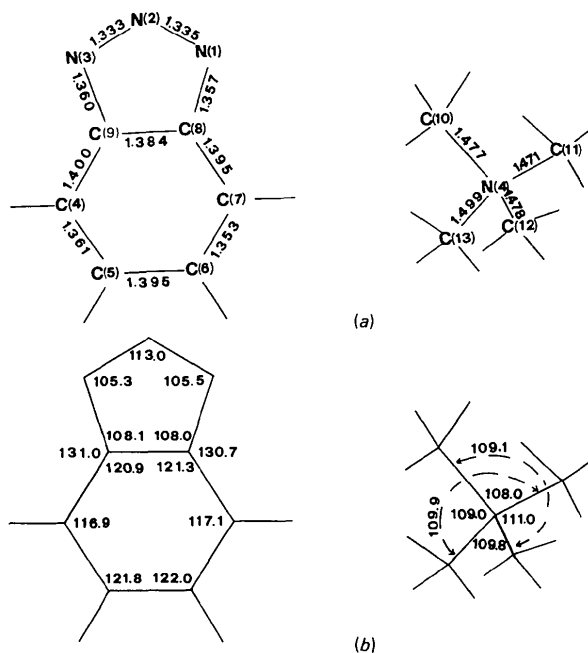

Fig. 1. (*a*) Bond lengths (Å) and numbering scheme. (*b*) Bond angles (°). Only values concerning the nonhydrogen atoms are shown. The ranges of the e.s.d.'s are: 0·004–0·006 Å (mean 0·0046 Å) for the bond lengths and 0·4–0·6° (mean 0·5°) for the bond angles.
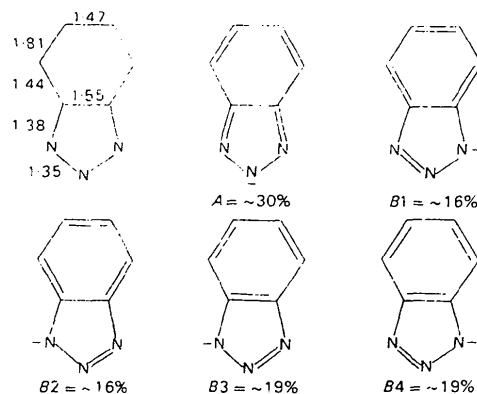
After the chemically equivalent bonds were averaged, Pauling's bond orders were derived from the bond-order–bond-length curves of Burke-Laing & Laing (1976); they are shown in Fig. 2 together with estimated contributions of the predominant resonance forms.

The larger contribution of the forms $B3$ and $B4$ compared with the $B1$ and $B2$ ones is a consequence of release of the constraint on the equivalence between these two pairs, in such a way as to reflect the shortening of the C(8)—C(9) bond compared with C(5)—C(6): a structural feature common to almost all X-ray analyses of benzotriazole systems (Giordano & Zagari, 1977, 1978; Giordano, 1980; Søtofte & Nielsen, 1981*a,b,c*, and references therein). This finding, though scarcely significant in each single case, becomes statistically meaningful owing to the consistency of the indications.

A comparison of the structures of the anion and the other benzotriazole systems displaying the same *mm* symmetry, namely the 1,3-benzotriazolium cation and the benzotriazol-2-yl residue, reveals a close resemblance in the π-electron distribution, as the weights of the quinoid forms of the six-membered ring and the benzenoid forms of the same ring are, in all cases, in the nearly constant ratio of 3:7 (Giordano & Zagari, 1978; Giordano, 1980). This result is in agreement with the presence of the same band at 270–280 nm in the UV spectrum (Dal Monte, Mangini, Passerini & Zauli, 1958).

Resonance forms indicate also a slightly larger negative charge on N(1) and N(3) in comparison with N(2), according to reactivity evidence showing that N(1) is a more nucleophilic position than N(2) (Benson & Savell, 1950).

The bond angles at the N atoms in the triazole ring (Table 2) are the most variable structural parameters in the benzotriazole systems, depending on changes in the bonding conditions and charge of the N atoms.

Table 2. *Comparison of the endocyclic angles (°) of the triazole ring in the free benzotriazolide anion with those in the benzotriazolido ions (bta) linked in coordination complexes and with those in other benzotriazole systems*

Average values for the assumed *mm* symmetry are given.

Molecular system	N(1)N(2)N(3)	N(2)N(1)C(8)	N(2)N(3)C(9)	N(1)C(8)C(9)	N(3)C(9)C(8)
Benzotriazolium ion [1]	105·1 (6)	112·8 (7)		104·6 (7)	
Benzotriazol-2-yl residue [2]	117·6 (66)	102·5 (7)		108·6 (7)	
Benzotriazol-1-yl residue [2]	107·7 (7)	111·4 (8)	108·9 (8)	103·7 (9)	108·3 (9)
Free benzotriazolide ion [3]	113·0 (5)	105·4 (5)		108·0 (5)	
[Ni₃(bta)₆(NH₃)₆] [4], [N(1),N(2)]-bidentate	112·4 (4)	106·4 (1)	106·0 (2)	106·9 (1)	108·4 (2)
[Ni₃(bta)₆(aa)₆] [5], [N(1),N(2)]-bidentate	112·7 (5)	105·5 (5)	106·7 (5)	106·5 (5)	108·5 (5)
[Tl(bta)] [6], tridentate	111·2 (5)	106·4 (4)	107·5 (4)	108·0 (4)	106·8 (4)
[Ir(bta)(CO)(PPh₃)₂] [7], [N(1)]-monodentate	110·4 (4)	107·8 (4)	106·8 (4)	106·1 (4)	108·8 (5)
[Zn₂(bta)₄] [8], [N(1),N(3)]-bidentate	109·8 (1)	108·3 (1)	108·4 (1)	107·0 (1)	106·6 (1)

References: (1) Giordano (1980); (2) Giordano & Zagari (1978); (3) this study; (4) Søtofte & Nielsen (1981c); (5) Meunier-Piret, Piret, Putzeys & Van Meerssche (1976) (aa = allylamine); (6) Reedijk, Roelofsen, Siedle & Spek (1979); (7) Brown, Ibers & Siedle (1978); (8) Søtofte & Nielsen (1981b).

N atoms in aromatic heterocycles are often indicated as 'pyridine' or 'pyrrole' N atoms according to whether they form, respectively, two or three σ bonds. The endocyclic angle at the 'pyrrole' N is larger than at the 'pyridine' one, in equivalent conditions. Thus, in the benzotriazolium cation the angles at N(1) and N(3), on the one hand, and at N(2), on the other, which are respectively 112·8 and 105·1°, correspond to these two different bonding states of the N atoms.

Conversely, in the benzotriazolide anion the angles at N(1) and N(3) decrease to 105·4° since they also become 'pyridine' N atoms, whereas the angle at N(2) widens to 113·0° in such a way as to soften the repulsive interaction between the negatively charged contiguous atoms. Finally, in the benzotriazol-2-yl residue the angle at N(2) becomes 117·6° as a result of the change of the central N to the 'pyrrole' type in the presence of the two other 'pyridine' N atoms in the ring.

The benzotriazolide anion can act as a ligand in organometallic compounds. The results of the X-ray analyses so far carried out show that the changes produced in the geometry of the anion by metal coordination are small and affect essentially the angles in the triazole ring (Table 2). In spite of this, they can be used to estimate the strength of the metal–ligand bond. Thus, from Table 2 we can infer that in the two [N(1), N(2)]-bidentate Ni complexes the metal–ligand bonds are weak, as the coordinated benzotriazolide retains virtually the same symmetry and the same geometry as the free group.
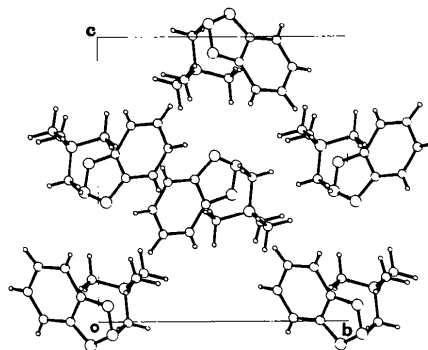

Fig. 3. Molecular packing viewed along **a.**

In the Tl complex, also, the benzotriazolide ligand seems to be only slightly modified.

On the other hand, in the [N(1), N(3)]-bidentate Zn complex the angles set is midway between those of the 1,3-benzotriazolium ion and the free benzotriazolide. The same situation occurs in the [N(1)]-monodentate Ir complex, where the values are intermediate between those of the free anion and the benzotriazol-1-yl residue.

The packing, shown in Fig. 3, is somewhat loose and consists of ranks of benzotriazolide anions arranged around screw axes parallel to **a.** They are inclined with respect to **a** at about 51° and are surrounded by positive ions. The benzotriazolide system is essentially planar, all atomic displacements from the best common plane being less than 0·015 Å.

The tetramethylammonium ion has the expected geometry with the C—H bonds in a staggered conformation.

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(2S,4S,5R)-2-Chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-Sulphide, C₁₀H₁₃ClNOPS*

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Abstract. m.p. $= 396-397$ K, $M_r = 261 \cdot 7$, orthorhombic, $P2_12_12_1$, $a = 9 \cdot 630$ (1), $b = 10 \cdot 318$ (5), $c = 12 \cdot 717$ (1) Å, $V = 1263 \cdot 58$ Å^3, $Z = 4$, $D_c = 1 \cdot 376$, $D_m = 1 \cdot 362$ Mg m^{-3} (in aqueous KI), $F(000) = 544$. Final $R = 0 \cdot 0451$ for 1326 observed reflections. The five-membered oxazaphospholidine ring exists in the crystal in an envelope conformation with C(4) deviating by $0 \cdot 500$ (4) Å upwards from the least-squares plane [N,P,O,C(5)].

Introduction. The configurations of the *cis* and *trans* isomers of 2-substituted 1,3,2-oxazaphospholidine 2-oxides, 2-sulphides and 2-selenides derived from (−)-ephedrine have been established by spectroscopic and chemical methods (Cooper, Hall, Harrison & Inch, 1977). The conversion of dialkyl(aryl) phosphoroanilidates into corresponding phosphates and phosphorothioates has been proved to be fully stereospecific and proceeding with retention of configuration at P in the case of chiral acyclic molecules as well as in 4-methyl-1,3,2-dioxaphosphorinane derivatives (Stec, Okruszek, Lesiak, Uznański & Michalski, 1976). 1,3,2-Oxazaphospholidines derived from (−)-ephedrine have been used as a model system to investigate the stereoselectivity of the above conversion when the P atom is incorporated into a five-membered ring.

The (2S,4S,5R)- and (2R,4S,5R)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulphides (hereafter referred to as BASTEL and TELBAS) have been prepared by reaction of phosphorothioyl chloride and (−)-ephedrine in the presence of triethylamine (Lesiak & Stec, 1978). The ¹H NMR spectra of both isomers and of derivatives obtained from them were not very helpful for stereochemical analysis possibly because of different conformations of oxaza-

phospholidine rings due to spatial requirements of exocyclic substituents at the P atom (Lesiak & Stec, 1978). Therefore, four compounds have been subjected to X-ray analysis to determine the conformation of the 1,3,2-oxazaphospholidine ring in the presence of different exocyclic substituents at the P atom and to describe the geometry of the ring. Moreover, the confirmation of absolute configuration by X-ray crystallography seemed essential as the assignments for BASTEL and TELBAS given by Lesiak & Stec (1978) were contrary to those given by Cooper *et al.* (1977, p. 1978). Here and in the following paper we report the crystal and molecular structures of this diastereoisomeric pair of compounds. We believe that this is the first example of a diastereoisomeric pair examined by X-ray techniques so far for a compound incorporating the 1,3,2-oxazaphospholidine ring.

Experimental. Spherical crystals, $\sim 0 \cdot 3$ mm in diameter, CAD-4 automated four-circle diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, $\mu = 5 \cdot 037$ mm^{-1}, 1371 reflections, room temperature, range $1° \leq 2\theta \leq 70°$, 1336 with $F_o \geq 3\sigma(F_o)$, no absorption correction, maximum $h,k,l = 11$, 12, 15; non-centrosymmetric direct methods (*SHELX* 76, Sheldrick, 1976).

The structure was refined by standard least-squares methods and difference electron density syntheses. Three cycles of full-matrix least-squares refinement using isotropic temperature factors resulted in $R = 0 \cdot 077$.

Introduction of anisotropic temperature factors required the application of a blocked full-matrix technique. All H atoms, except those belonging to methyl groups, were located in a weighted difference Fourier synthesis based on reflections with sin $\theta/\lambda \leq 0 \cdot 3$ Å^{-1}. The methyl H atoms were generated with the methyl groups assumed to be staggered (C—H

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* Conformation of the 1,3,2-Oxazaphospholidine Ring. I.

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