

would be low. Ideal unit-cell dimensions are shown in Table 6.

Finally it should be noted that Fig. 5, by emphasizing the similarities of packing, also offers a logical explanation for red and blue bronzes existing as parallel domains within certain crystals. We believe that this intergrowth between two or more structures could persist at the unit cell level, and perhaps for this reason a high degree of structure refinement is not achieved, and the questions of exact composition remain largely unresolved.

We wish to express our appreciation to Dr J.C.B. White for the use of his version of the ORFLS program on the IBM 7044 computer at Melbourne University.

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The Crystal and Molecular Structure of 3,3'-Bi-2-isoxazoline

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The structure of 3,3'-bi-2-isoxazoline, $C_6H_8N_2O_2$, a novel product of the reaction of ethylene and nitrogen dioxide, has been determined from three-dimensional scintillation-counter $Cu K\alpha$ diffraction data. The crystals are orthorhombic with space group $Iba2$; four molecules per unit cell. The unit cell constants are: $a = 8.92_2$, $b = 10.50_0$, $c = 7.04_2$ Å.

The positional and anisotropic thermal parameters were refined by full-matrix least-squares methods.

The molecule consists of two bridged five-membered isoxazoline rings. The conjugated bridging C-C bond was found to be 1.42 ± 0.02 Å. The molecule is essentially planar.

Introduction

One of the hitherto unreported products of the reaction of ethylene and nitrogen dioxide in anhydrous carbon tetrachloride is 3,3'-bi-2-isoxazoline, $C_6H_8N_2O_2$. In contrast to the previously known products of the reaction, which are all either unstable or explosive (Levy & Rose, 1947; Levy & Scaife, 1946; Levy, Scaife & Smith, 1946), the new product is most unusual for its inertness to common reagents and its marked thermal stability.

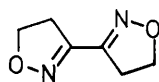
Although several substituted bi-isoxazolines are described in the literature (Quilico & Grunanger, 1952; Quilico, Grunanger & Mazzini, 1952), this appears to be the first parent compound prepared in any of the isomeric bi-isoxazoline series.

From the consideration of the chemical and physical properties, including infrared and ultraviolet absorption data, and nuclear magnetic resonance (Soffer, 1966), it is evident that the molecule is heterocyclic with both the oxygen and nitrogen in the ring. These data indicated either (I) or (II) as possible structures. Both satisfy the diffraction data requirements of a two-fold axis and near planarity. The preliminary X-ray structure analysis as reported by Bednowitz & Fan-

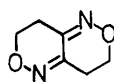
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kuchen (1963) unambiguously established that the compound is represented by formula (I).



(I)



(II)

Experimental

X-ray data

A small crystal of dimensions $0.3 \times 0.2 \times 0.3$ mm was used to obtain complete three-dimensional data. From rotation and Weissenberg photographs the approximate lattice dimensions were obtained and the diffraction aspect determined. More precise lattice constants were measured on a counter diffractometer using high order axial reflections. The intensities of 332 observable reflections were measured at 25°C by using a full-circle goniometer single-crystal orienter on a Nor-elco wide range diffractometer with copper radiation and balanced Ross filters. No absorption corrections were necessary.

Unit cell and space group

3,3'-Bi-2-isoxazoline crystallizes from an ethanol solution in colorless, orthorhombic prisms. Between crossed polaroids, the prisms were found to show parallel extinction along the long axis designated as the c axis. The lattice parameters are: $a = 8.92_2$, $b = 10.50_0$, $c = 7.04_2$ Å; $\rho_{\text{obs}} = 1.409$ g.cm $^{-3}$, $\rho_{\text{calc}} = 1.411$ g.cm $^{-3}$, with four molecules per unit cell. Data were obtained with Cu $K\alpha$ radiation. The estimated error in the lattice constants is ± 0.004 Å.

At approximately -120°C the crystal becomes twinned while undergoing a phase transition to a body-centered monoclinic lattice. (The axial designations remain the same, *i.e.* the b axis in the orthorhombic form becomes the unique axis in the low-temperature phase.) The cell dimensions are slightly decreased as determined from precession photographs. At -150°C , $a = 8.92$, $b = 10.45$, $c = 6.95$ Å, $\beta = 95.0^\circ$, $\rho_{\text{calc}} = 1.432$ g.cm $^{-3}$. When brought back to room temperature the crystal rapidly anneals. The phase change is completely reversible and the crystal can be raised and lowered in temperature repeatedly. The twin boundary is either the ab plane or the ac plane or both, giving a mixed twinning. The transformation is probably due to a slight shift in the molecular orientation which results in a decrease in the interplanar molecular spacing as shown by a relatively large contraction in the c direction.

Systematic absences include: h and l odd for $h0l$, k and l odd for $0kl$, $h+k+l$ odd for hkl . Either $Iba2$ or $Ibam$ satisfies the requirements of the diffraction aspect. As there are only four molecules per unit cell, both space groups require the molecule to be in a special position with at least twofold symmetry. The choice

of $Iba2$ (No.45) resulted in a successful structure determination. The asymmetric unit contains one half of the molecule and all atoms are in eightfold general positions $8(c)$: $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + (x,y,z; \bar{x}, \bar{y}, z; \bar{x}, y, \frac{1}{2} + z; x, \bar{y}, \frac{1}{2} + z)$ (*International Tables for X-ray Crystallography*, 1952).

Structure determination

Consideration of the symmetry of the space group and the length of the c axis requires any double ring skeleton to be almost planar and approximately parallel to the C face.

Patterson projections along the a , b , and c axes also indicate that the molecule lies close to the plane perpendicular to the c axis, and in addition require the atoms to be arranged so that the majority of interatomic vectors are parallel to either a or b . An attempt at the structure determination was first made assuming a molecule consisting of two fused six-membered rings (II). The Patterson maps were compared to vector diagrams constructed from the fused six-membered double ring skeleton. The results indicated the molecule would have to lie with its long axis parallel to b . Preliminary computations were done with an optical analog computer, the von Eller Photosommateur. Signs for the $hk0$ reflections were determined by examining the Fourier transforms of eight unit cells whose contents had been projected along the c axis. The technique of using the von Eller Photosommateur to obtain signs in this manner is described by Amendola (1962). The plane symmetry of the xy projection is identical in $Iba2$ and $Ibam$. Iterative cycles of two-dimensional structure factor and electron density calculations, using IBM 650 programs by Shiono (1957), were applied until the residual, R , was stationary at 40%, where $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. This value suggested that some of the atoms were probably in correct positions, but spurious peaks and distorted bond distances indicated the structure was not completely correct. Bragg-Lipson contour maps were drawn for a few reflections of low order, 110, 220, 200, 020, and it was quickly seen that structure (II) could not account for their intensities.

The bridged double five-membered ring structure (I) was then tried. For this structure the best agreement between the vector map and the Patterson maps was obtained when the long axis of the molecule was parallel to the a axis. With this orientation the central six atoms are identical with the central frame of the previous model. Similar iterative computations with the new model lowered the R below 24% for the $hk0$ reflections. This high value of the residual was due to extensive superposition of atoms in the xy projection. The double five-membered rings shown in Fig.1 are not *one* molecule but a projection of *two*, almost directly superposed. A three-dimensional structure factor calculation using isotropic temperature factors resulted in a residual of 37% for the observed reflections. Here, the structure factors were calculated on the basis of

Table 1. Atomic and thermal parameters in 3,3'-bi-2-isoxazoline

Atomic parameters (e.s.d. $\times 10^5$)						
Atom	x	e.s.d.	y	e.s.d.	z	e.s.d.
C(1)	0·07879	46	0·00911	37	0·0	90
C(2)	0·15868	56	0·13714	41	0·00122	90
C(3)	0·31741	75	0·09459	50	0·00222	90
N(4)	0·16570	42	-0·08563	37	0·00354	80
O(5)	0·31568	35	-0·04425	30	0·00720	75
H(6)	0·19088	760	0·17603	700	0·14786	1000
H(7)	0·11971	770	0·20157	630	-0·12597	1000
H(8)	0·34486	880	0·11389	610	0·18149	1000
H(9)	0·38231	840	0·12093	680	-0·09198	1000

Thermal parameters (values $\times 10^5$)						
Temperature factor = $\exp \{ -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \}$						
Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	1559	790	2834	37	649	534
e.s.d.	52	33	109	84	426	390
C(2)	1604	813	4120	-417	495	-762
e.s.d.	78	44	215	84	636	352
C(3)	1695	1067	5500	-205	-353	798
e.s.d.	94	56	278	102	678	543
N(4)	1558	839	4702	92	-210	-1734
e.s.d.	63	40	210	71	430	292
O(5)	1527	1172	6094	18	-1192	-493
e.s.d.	54	42	220	64	480	406
H(6-9)	B = 1·9 Å ² ,	e.s.d. = 1·5				

Table 2. Comparison of observed and calculated structure factors ($\times 10$)

H	K	L	FoBS	FcAL	H	K	L	FoBS	FcAL	H	K	L	FoBS	FcAL	H	K	L	FoBS	FcAL	H	K	L	FoBS	FcAL					
0 4	569	553	8 5	18	19	12 2	14	13	3 7	7* 10	9 4	8* 20	6 1	97	99	9 4	8* 20	6 1	97	99	9 4	8* 20	6 1	97	99				
0 6	162	169	9 0	58	76	3 1	0	159	164	4 0	120	104	10 1	14	26	6 3	6	6	60	64	7 0	32	31	7 0	32	31			
0 8	46	44	9 2	67	69	1 2	82	81	4 4	19	27	11 0	7*	10	7 2	25	25	25	25	25	7 4	16	16	7 4	16	16			
2 2	851	795	4 4	44	45	1 4	15	21	4 6	9*	10	6 0	0	0	343	357	78	8 1	28	21	8 1	28	21	8 1	28	21			
2 4	314	311	10 1	72	65	1 6	9*	7	5 1	18	22	0 2	247	247	8 3	7*	13	13	13	13	9 0	24	26	9 0	24	26			
2 6	90	88	10 5	34	31	1 8	25	4	5 3	30	32	0 4	94	101	9 0	24	26	26	26	9 2	23	21	9 2	23	21				
2 8	8*	25	11 0	33	34	2 1	67	84	5 5	27	29	0 6	24	27	8 3	7*	13	13	13	13	9 2	23	21	9 2	23	21			
4 0	256	249	11 0	34	39	2 1	67	84	5 5	27	29	0 4	94	101	9 0	24	26	26	26	9 2	23	21	9 2	23	21				
4 2	146	133	11 2	29	32	2 3	27	22	5 7	7*	14	0 6	24	27	8 3	7*	13	13	13	13	9 2	23	21	9 2	23	21			
4 4	39	41	11 4	23	21	2 5	8*	8	6 0	7*	1	1 1	26	24	8 3	7*	13	13	13	13	9 2	23	21	9 2	23	21			
4 6	8*	19	12 1	8*	6	2 7	8*	3	6 2	9*	8	1 3	15	19	8 0	0	187.	194	194	194	8 0	0	187.	194	8 0	0	187.	194	
4 8	7*	11	3 0	395	397	3 2	272	270	6 4	9*	6	1 5	8*	6	0 2	152	156	156	156	0 2	152	156	0 2	152	156	0 2	152	156	
6 0	120	120	3 2	272	270	6 6	8*	5	7 1	156	148	2 2	56	55	0 4	77	82	82	82	0 4	77	82	0 4	77	82	0 4	77	82	
6 2	92	91	0 4	166	150	3 5	108	103	7 1	74	75	2 4	13	9	1 1	8*	7	7	7	1 1	8*	7	1 1	8*	7	1 1	8*	7	
6 4	30	35	0 6	37	32	3 6	30	34	7 3	74	75	2 4	13	9	1 3	8*	9	9	9	1 3	8*	9	1 3	8*	9	1 3	8*	9	
6 6	8	16	0 8	8*	5	4 1	72	68	7 5	23	25	2 6	8*	9	1 5	7*	5	5	5	1 5	7*	5	1 5	7*	5	1 5	7*	5	
8 0	55	51	1 1	42	43	4 3	51	49	8 0	33	38	3 1	26	24	2 0	131	129	129	129	2 0	131	129	2 0	131	129	2 0	131	129	
8 2	56	55	1 3	7*	10	4 5	18	18	8 2	35	34	3 3	8*	3	2 2	100	103	103	103	3 3	8*	3	2 2	100	103	3 3	8*	3	
8 4	49	49	1 5	7*	3	4 7	7*	5	8 4	26	24	3 5	8*	4	2 4	46	53	53	53	3 5	8*	4	2 4	46	53	3 5	8*	4	
8 6	22	28	1 7	6*	7	5 0	115	108	9 1	137	134	4 0	212	208	3 1	40	34	34	34	4 0	212	208	3 1	40	34	3 1	40	34	
10 0	46	47	2 0	247	231	5 2	119	122	9 3	85	88	4 2	168	166	3 3	25	23	23	23	4 2	168	166	3 3	25	23	3 3	25	23	
10 2	39	43	2 2	156	161	5 4	69	71	9 5	35	37	4 4	95	100	3 5	6*	12	12	12	4 4	95	100	3 5	6*	12	3 5	6*	12	
10 4	23	36	2 4	45	43	5 6	27	22	10 0	11	9	4 6	45	46	4 0	14	10	10	10	4 6	45	46	4 0	14	10	4 0	14	10	
12 0	36	37	2 6	9*	9	6 1	91	92	10 2	9*	13	5 1	78	73	4 2	9*	13	13	13	5 1	78	73	4 2	9*	13	4 2	9*	13	
12 2	39	37	2 8	11	7	6 3	62	56	10 4	7*	13	5 3	41	46	4 4	8*	13	13	13	5 3	41	46	4 4	8*	13	4 4	8*	13	
			3 1	139	150	6 5	23	23	11 1	17	7	5 5	8*	15	5 1	54	57	57	57	6 0	160	153	6 2	8*	24	6 0	160	153	
1 0	305	333	3 3	27	35	6 7	7*	8	5 1	0	303	291	6 0	160	153	6 2	8*	24	24	6 0	160	153	6 2	8*	24	6 0	160	153	
1 2	257	263	3 5	7*	15	7 0	67	67	5 1	0	303	291	6 2	121	127	5 3	42	41	41	6 2	121	127	5 3	42	41	5 3	42	41	
1 4	137	127	3 7	8*	5	7 2	54	58	1 2	220	221	6 4	75	73	6 0	30	29	29	29	6 4	75	73	6 0	30	29	6 0	30	29	
1 6	57	58	4 0	290	295	7 4	25	30	1 4	98	100	7 1	56	51	7 1	14	10	10	10	7 1	56	51	7 1	14	10	7 1	14	10	
1 8	27	23	4 2	216	210	7 6	8*	8	1 6	28	35	7 3	36	31	7 3	6*	5	5	5	7 3	36	31	7 3	6*	5	7 3	6*	5	
2 1	112	126	4 4	114	104	8 1	36	86	2 1	6*	22	7 5	13	10	8 0	7*	0	0	0	2 1	6*	22	7 5	13	10	8 0	7*	0	
2 5	7*	25	4 6	42	43	8 3	51	60	2 3	7*	13	8 0	43	49	8 0	12	22	22	22	4 6	42	43	8 3	51	60	2 3	7*	13	
2 7	3*	8	5 1	0*	23	8 5	28	29	2 5	8*	6	8 2	41	44	9 1	0	12	22	22	5 1	0*	23	8 5	28	29	2 5	8*	6	
3 0	5*	13	5 3	16	33	9 0	26	30	2 7	7*	5	8 4	26	30	1 2	12	22	22	22	5 3	16	33	9 0	26	30	2 7	7*	5	
3 2	27	32	5 5	8*	24	9 2	31	36	3 0	225	224	9 1	20	16	1 4	9*	15	15	15	5 5	8*	24	9 2	31	36	3 0	225	224	
3 4	32	44	5 7	8*	11	9 4	46	34	3 2	173	165	9 3	9*	9	2 1	13	9	9	9	5 7	8*	11	9 4	46	34	3 2	173	165	
3 6	17	25	6 0	21	221	10 1	36	36	3 4	83	78	10 0	25	28	2 3	7*	6	6	6	6 0	21	221	10 1	36	36	3 4	83	78	
3 8	8*	31	6 2	167	178	11 0	3	29	25	3 6	29	31	10 2	20	28	3 0	39	34	34	6 2	167	178	11 0	3	29	25	3 6	29	
4 1	397	408	6 4	90	90	11 0	8*	4	4 1	168	174	7 1	0	40	38	3 2	30	27	27	6 4	90	90	11 0	8*	4	4 1	168	174	
4 3	174	172	6 6	9*	33	12 1	7*	5	4 3	92	100	7 1	0	40	38	3 4	15	13	13	6 6	9*	33	12 1	7*	5	4 3	92	100	
4 5	48	52	7 1	211	247	13 1	128	122	5 0	110	95	1 4	9*	10	4 3	7*	14	14	14	7 1	211	247	13 1	128	122	5 0	110	95	
4 7	11	14	7 3	128	122	4 0	0	495	483	5 0	110	95	1 4	9*	10	4 3	7*	14	14	7 3	128	122	4 0	0	495	483	5 0	110	95
5 0	129	117	7 5	90	49	0 2	378	304	5 2	78	75	1 6	7*	4	5 0	18	26	26	26	7 5	90	49	0 2	378	304	5 2	78	75	
5 2	69	59	8 0	88	77	0 4	131	128	5 4	43	44	2 1	27	21	5 2	26	21	21	21	8 0	88	77	0 4	131	128	5 4	43	44	
5 4	27	38	8 2	60	60	0 6	34	47	5 6	23	20	2 3	8*	9	6 1	16	16	16	16	8 2	60	60	0 6	34	47	5 6	23	20	
5 6	19	23	8 4	32	34	1 1	30	20	6 1	136	130	2 5	8*	2	6 1	16	16	16	16	8 4	32	34	1 1	30	20	6 1	136	130	
6 1	304	304	8 6	13	17	1 3	20	19	6 3	83	83	3 0	107	92	10 0	0	8*	0	0	8 6	13	17	1 3	20	19	6 3	83	83	
6 3	157	166	9 1	22*	221	1 5																							

Iba2 with the central bridging carbon atoms fixed at $z=0$. A full-matrix least-squares refinement, using an IBM 7094 machine (Okaya, 1963) was then attempted. Refinement proceeded to an R of 30% and became stationary. This was due to a pseudo-minimum in R , resulting from good agreement for the even l layers

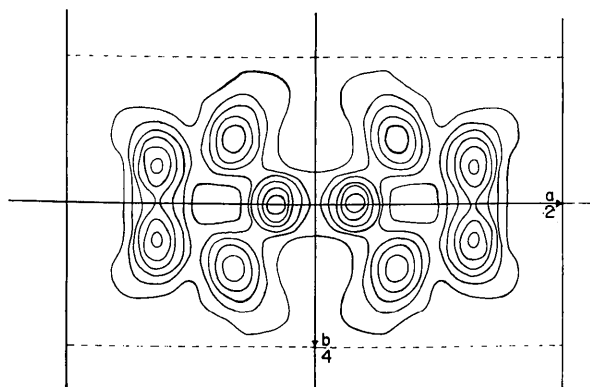


Fig. 1. Electron density function projected down the c axis.

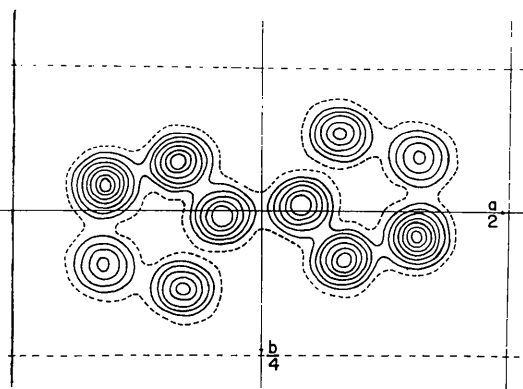


Fig. 2. Three-dimensional electron density function; section at $z=0$, after refinement. Contours are drawn at intervals of $1 \text{ e.}\text{\AA}^{-3}$ starting at $1 \text{ e.}\text{\AA}^{-3}$.

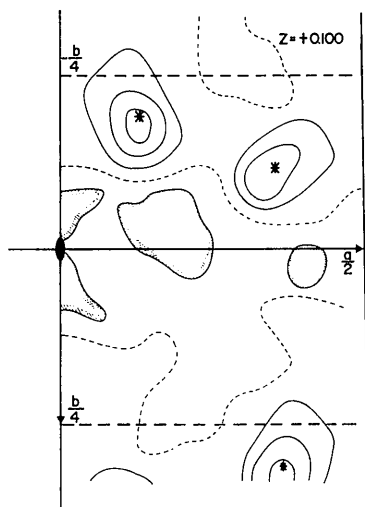


Fig. 3. Three-dimensional difference synthesis showing hydrogen atoms; section at $z=0.100$.

but gross disagreement for the odd l layers. Interchanging the z coordinates of some of the atoms between 0 and $\frac{1}{2}$ led to rapid refinement of the three-dimensional structure. The atomic scattering factors used were those of Freeman (1959).

The five heavy atoms were refined with anisotropic temperature factors. The hydrogens were refined with a single isotropic temperature factor applying to all of them. The weighting scheme was divided into three parts: for the strong reflections (> 25) the weight was inversely proportional to $|F_{\text{obs}}|^2$; for the very weak and unobserved reflections (< 0.9) the weight was zero; and for the moderate intensities the weight was proportional to $|F_{\text{obs}}|$.

The final residual was 8.0% including the weak and unobserved reflections. Several intense low order reflections seemed to suffer from extinction errors and were discarded in the final refinement.

Table 1 lists the atomic and thermal parameters of the atoms with their e.s.d.'s as determined from the last cycle of least-squares refinement. The final shifts of the heavy atoms were not more than one-fifth of the e.s.d.'s. Carbon(1) was reset to $z=0$ in order to fix the origin. The e.s.d.'s for the z coordinates are approximate values relative to the reset coordinates.

The comparison of observed and calculated structure factor magnitudes is given in Table 2. Of the 328 reflections listed in Table 2, 83 were either unobserved or too weak to measure reliably. These reflections were given an arbitrary observed intensity two-thirds of the value of the weakest measured reflection. These reflections are distinguished by the symbol* next to the F_{obs} value.

The phases determined from the final least-squares refinement were used for computing the three-dimensional electron density function (see Fig. 2 for the section through the molecule). An $(F_o - F_c)$ synthesis, where only the contributions of the heavier atoms were included in F_c , was computed. A section through the position of the hydrogen atoms ($z=0.100$) is shown in Fig. 3. Two of the hydrogen atoms are clearly evident in this section. Another section through the plane of the heavy atoms indicated no peaks of height greater than $\frac{1}{2} \text{ e.}\text{\AA}^{-3}$.

In Fig. 4 the bond lengths and angles are indicated with their respective e.s.d.'s. Also included are some of the shorter intermolecular contacts. The Fourier summation and bond distance programs were those reported by Okaya (1963).

Discussion

The X-ray structure determination shows that 3,3'-bi-2-isoxazoline is essentially a planar molecule. The planarity would tend to be maintained by resonance interaction in the conjugated system. The oxygen atoms are out of the plane by less than 0.04 \AA . This is probably due to a slight puckering of the saturated portion of the ring.

There is some shortening in both of the C-C single bonds in the rings, but this is in accord with values found for other five-membered cyclic systems. The shortening by resonance of the central bond in the conjugated dioxime ether is worthy of note. The resonance interaction would help to keep the system in the more stable transoid form in which it is found to exist in the solid state. The ultraviolet absorption spectrum is very similar to that of dimethylglyoxime dimethyl ether, and both compounds have similar absorption in the significant infrared regions.

The full circle goniometer used in this work was a prototype made available to us by Electronics and Alloys, Inc. Ridgefield, N.J.

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Solution of the Phase Problem in Centrosymmetric Structures with Heavy Atoms in Special Positions

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The number of the signs of unitary structure factors of a centrosymmetric structure determined by the presence of heavy atoms in special positions is expressed in terms of probability relationships. Some methods for complete solution of the phase problem in this case are considered.

Introduction

The 'heavy-atom' method of solving centrosymmetric crystal structures has been proved to be most promising in the determination of molecular structures. A criterion for deciding the degree of resolution of the crystal structure by the heavy-atom method was given by Luzzati (1953), Woolfson (1956) and Sim (1957).

The present paper deals with a case when the heavy atoms of a centrosymmetric structure are in special positions.

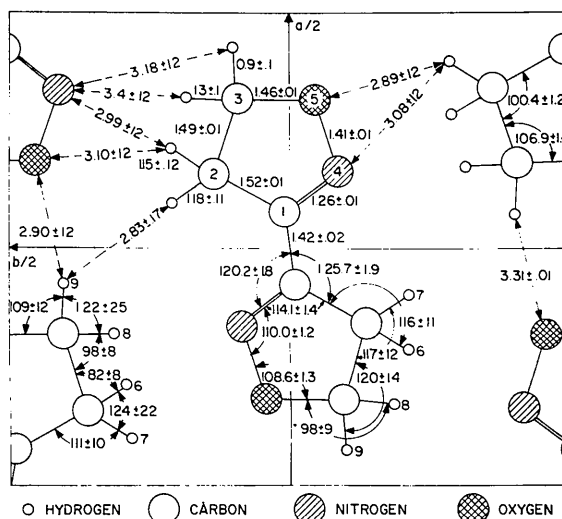


Fig. 4. Bond distances and angles in 3,3'-bi-2-isoxazoline.

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Basic relations

Let heavy atoms occupy special positions whose multiplicity α is lower than the multiplicity of the general positions. Further let us suppose that the following equation is valid for indices h_1, h_2, h_3 :

$$\frac{h_1}{u_1} + \frac{h_2}{u_2} + \frac{h_3}{u_3} = \sum_{s=1}^3 \frac{h_s}{u_s} = \mathbf{h} \cdot \mathbf{r} = \text{integer} \quad (1)$$

$1/u_s$ are the fractional coordinates of the heavy atoms, \mathbf{h} is the reciprocal lattice vector, \mathbf{r} is the direct lattice vector.