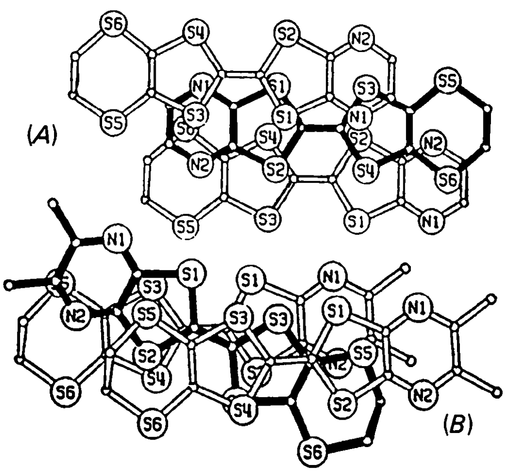

Fig. 4. Projections showing overlap of donors.

tacts (Williams & Carneiro, 1986). In the present structures as with the $(TMTSF)_2X$ salts, while there is no dimerization, the stacks are in phase, which leads to the two-dimensional 'sheet network' of S···S contacts here and Se···Se contacts in $(TMTSF)_2X$ salts (Williams & Carneiro, 1986).

Substitution of the methyl groups (*B*) for the pyrazino hydrogen atoms (*A*) has had the following effects on the packing of the donor molecules: (*a*) the relationship of the neighbors in the plane of the molecule is centrosymmetric in (*A*) and translational in (*B*) (Fig. 2); (*b*) there is better stacking in (*B*) (Fig. 4); and (*c*) there are better intra- and interstack S···S contacts in (*B*) (Figs. 2 and 3). These are dramatic changes since it is known (Williams & Carneiro, 1986) that minute differences in crystallographic structure are translated into differences in physical behavior.

The I_3^- ions are probably involved in weak van der Waals interactions with the hydrogen atoms but because of the anion disorder we will not discuss them here. The major reason for this anion disorder is probably their mode of packing. They pack in a head-to-tail arrangement almost on a straight line along the *b* axis which probably is not conducive to pinning them down. Preliminary conductivity measurements give $\sigma_{RT} \simeq 1$–$50\ \Omega^{-1}\,cm^{-1}$.

AT would like to thank Bob Bau and the Chemistry Department of the University of Southern California for their hospitality and for use of their facilities.

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Acta Cryst. (1988). C**44**, 128–132

Structures of the Conducting Salts of Pyrazinoethylenedithiotetrathiafulvalene (PEDTTTF) and [4,5-*b*]Pyridinoethylenedithiotetrathiafulvalene ([4,5-*b*]PEDTTTF): α-$(PEDTTTF)_2IBr_2$ and α-$([4,5\text{-}b]PEDTTTF)_2IBr_2$

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Abstract. (I): Bis{2-(dithiolo[4,5-*b*]dithiin-2-ylidene)-dithiolo[4,5-*b*]pyrazinium} dibromoiodide, $(C_{10}H_6N_2S_6)_2IBr_2$, $M_r = 979.86$, triclinic, $P\bar{1}$, $a = 8.847$ (1), $b = 5.671$ (1), $c = 15.818$ (2) Å, $\alpha = 98.44$ (1), $\beta = 89.66$ (1), $\gamma = 107.13$ (1)°, $V = 749.6$ Å^3, $Z = 1$, $D_m = 2.20$, $D_x = 2.170$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1.54178$ Å, $\mu = 192.03$ cm^{-1}, $F(000) = 475$, $T = 296$ (2) K. (II): Bis{2-(dithiolo[4,5-*b*]dithiin-2-ylidene)dithiolo[4,5-*b*]-

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* To whom correspondence should be addressed.

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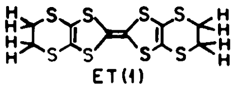
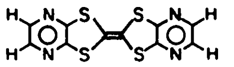
pyridinium} dibromoiodide, $(C_{11}H_7NS_6)_2IBr_2$, $M_r = 977{\cdot}86$, triclinic, $P\bar{1}$, $a = 7{\cdot}308\,(1)$, $b = 6{\cdot}475\,(1)$, $c = 16{\cdot}895\,(2)$ Å, $\alpha = 92{\cdot}68\,(1)$, $\beta = 92{\cdot}31\,(1)$, $\gamma = 105{\cdot}83\,(1)°$, $V = 767{\cdot}23$ Å^3, $Z = 1$, $D_m = 2{\cdot}12$, $D_x = 2{\cdot}116$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54178$ Å, $\mu = 187{\cdot}41$ cm^{-1}, $F(000) = 475$, $T = 296\,(2)$ K. Final R values are 0·031 (I) and 0·033 (II) for 2224 and 2491 reflections. Cations in both structures pack side by side, in a planar arrangement, through S···S and S···N contacts the shortest of which are S···S = 3·427, S···N = 3·331 (I); S···S = 3·336 Å (II). There is also partial stacking and there are intrastack contacts, the shortest being S···S = 3·748 (I); S···S = 3·468, S···N = 3·488 Å (II). Small modifications on the donor (BEDT-TTF, also known as ET) lead to strikingly different packing of these donors compared with $(ET)_2X$ salts. Changing I_3^- to the smaller IBr_2^- leads to good H···Br contacts which help to pin down the IBr_2^- positions while I_3^- is disordered.

Introduction. Following the discovery (Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984) and confirmation (Williams, Emge, Wang, Beno, Copps, Hall, Carlson & Crabtree, 1984) of superconductivity at ambient pressure in the first sulfur-based organic metal, β-$(ET)_2I_3$, attempts are being made to modify the structural and physical properties of this material. One approach is to substitute the triiodide anion systematically by various other trihalide anions of differing sizes and polarizabilities (Leung, Emge, Schultz, Beno, Carlson, Wang, Firestone & Williams, 1986). Another approach is to modify the cation. ET (1) has been modified to (2) (Terzis, Hountas & Papavassiliou, 1986), to (3) and (5) (Psycharis, Hountas, Terzis & Papavassiliou, 1988), and, in this study, further modified to (4). At the same time IBr_2^- was used, instead of the I_3^- used in the previous study (Psycharis, Hountas, Terzis & Papavassiliou, 1988), in an attempt to avoid the disorder in the anion and to be able to look at its hydrogen environment more accurately.



ET(1)



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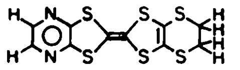
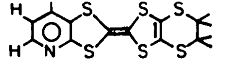
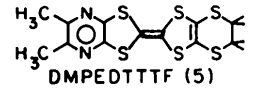


PEDTTTF (3)



[4,5-b]PEDTTTF (4)



DMPEDTTTF (5)

Experimental. Title compounds were prepared by electrocrystallization of the donor ($1{\cdot}55 \times 10^{-3}M$) and Bu_4NIBr_2 ($5 \times 10^{-3}M$) in CH_2Cl_2, using platinum electrodes, at 1 μA cm^{-2} and 295 K. Crystal color is metallic reddish-black. The donors were prepared according to Papavassiliou, Yiannopoulos and Zambounis (1987). Crystals are elongated hexagonal plates (I) and long parallelepipeds with a cross section of a distorted hexagon (II). Data crystals were 0·07 × 0·27 × 0·31 mm (I) and 0·08 × 0·12 × 0·30 mm (II). D_m by flotation in $CHCl_3/C_2H_2Br_4$. Intensity data collected on a Syntex $P2_1$ computer-controlled diffractometer. Lattice parameters from 15 intermediate

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	(I)				(II)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
I	0	0	0	38·2 (2)	0	0	0	53·5 (2)
Br(1)	7599·0 (6)	1993 (1)	139·0 (3)	68·3 (3)	−1920 (1)	2349 (1)	810·0 (3)	80·4 (4)
S(1)	10960 (1)	−7423 (2)	4489·2 (5)	34·6 (5)	2164 (1)	1963 (1)	5093·5 (5)	36·8 (5)
S(2)	132144 (1)	−2394 (2)	4502·6 (5)	34·1 (4)	2537 (1)	6515 (1)	5589·7 (6)	40·2 (5)
S(3)	7583 (1)	−2227 (2)	3713·2 (5)	32·8 (4)	2926 (2)	3246 (1)	3313·8 (5)	39·9 (5)
S(4)	5300 (1)	−7171 (2)	3672·6 (5)	35·5 (5)	3459 (1)	7787 (1)	3790·5 (6)	40·1 (5)
S(5)	6666 (1)	−1468 (2)	2021·4 (6)	44·8 (5)	3728 (2)	3941 (2)	1644·4 (6)	64·8 (7)
S(6)	3801 (1)	−7317 (2)	2013·0 (7)	49·3 (6)	4462 (2)	9362 (2)	2222·8 (6)	59·1 (7)
N(1),N	267 (4)	6967 (6)	6997 (2)	40 (2)	1279 (5)	843 (5)	6561 (2)	39 (2)
N(2),C(11)	−1891 (4)	2188 (6)	6982 (2)	41 (2)	1589 (6)	5160 (7)	7101 (3)	45 (2)
C(1)	244 (5)	5584 (8)	7629 (2)	47 (2)	975 (6)	1426 (7)	7309 (3)	49 (2)
C(2)	−795 (5)	3274 (8)	7613 (2)	46 (2)	1138 (6)	3471 (8)	7600 (3)	51 (2)
C(3)	−806 (4)	5881 (6)	6376 (2)	30 (2)	1734 (5)	2511 (6)	6081 (2)	33 (2)
C(4)	−1881 (4)	3536 (6)	6367 (2)	32 (2)	1906 (5)	4653 (6)	6320 (2)	36 (2)
C(5)	−2534 (4)	5009 (6)	4993 (2)	27 (2)	2629 (5)	4614 (5)	4834 (2)	34 (2)
C(6)	−3168 (4)	5176 (6)	4224 (2)	29 (2)	2985 (5)	5162 (5)	4081 (2)	33 (2)
C(7)	−3668 (4)	6613 (6)	2802 (2)	33 (2)	3578 (6)	5072 (6)	2583 (2)	39 (2)
C(8)	−4752 (4)	4325 (6)	2790 (2)	33 (2)	3841 (6)	7163 (6)	2804 (2)	40 (2)
C(9*A*)	4860 (10)	−2890 (16)	1380 (6)	46 (6)	4460 (10)	6270 (10)	1062 (4)	63 (3)
C(9*B*)	5536 (9)	−3570 (14)	1124 (4)	42 (4)	3144 (22)	5870 (17)	1016 (9)	64 (5)
C(10*A*)	4390 (16)	−5650 (16)	1133 (6)	40 (7)	3581 (10)	8027 (10)	1281 (4)	57 (3)
C(10*B*)	3900 (10)	−4980 (17)	1344 (6)	43 (5)	4470 (26)	8043 (24)	1261 (7)	73 (5)

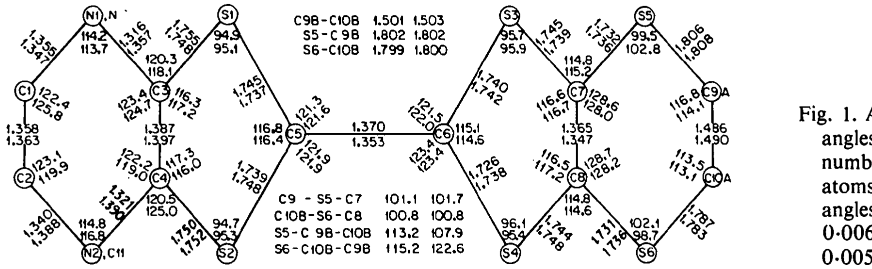


Fig. 1. Atom numbering and bond distances and angles. Top numbers refer to (I), bottom numbers refer to (II). E.s.d.'s involving S atoms: 0·003–0·004 Å for distances, 0·2° for angles; involving the disordered C(9)–C(10): 0·006–0·009 Å, 0·5–1·1°; all others: 0·004–0·005 Å, 0·3–0·4°.

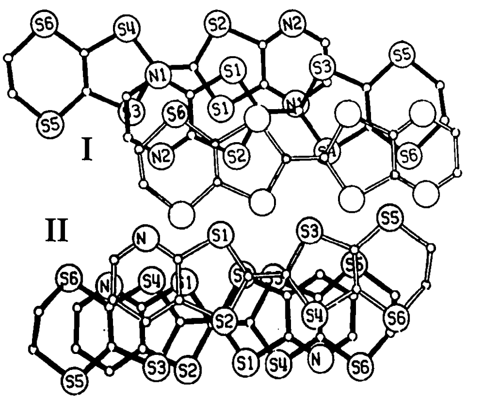


Fig. 2. Planar arrangement of donors with S···S and S···N contacts.

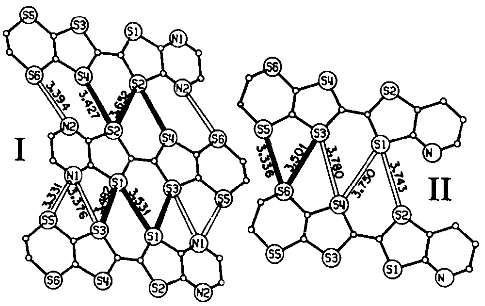
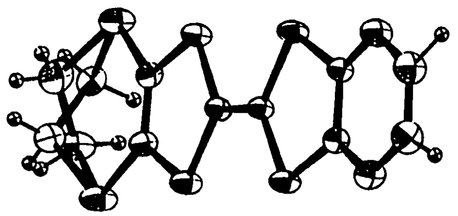


Fig. 3. Projections showing overlap of donors.

2θ reflections. Data in range $2\theta \leq 120°$ [range of $hkl = 0 \to 9, -6 \to 6, -17 \to 17$ (I); $-7 \to 0, -7 \to 7, -17 \to 17$ (II)], $\omega/2\theta$ scan mode, scan speed 2–15° (2θ) min^{-1}, scan width 1·8° (2θ) plus α_1–α_2 divergence. Three reflections monitored periodically showed < 3·0% intensity fluctuation. Lorentz–polarization and analytical absorption corrections applied [$T_{\min}/T_{\max}$ 0·06/0·39 (I), 0·05/0·19 (II)] with *SHELX*76 (Sheldrick, 1976). Data collected/unique/R_{int}, 2405/2224/0·016 (I), 4448/2491/0·011 (II). All data used. Positions for I and Br deduced from Patterson map, remainder from difference map. Full-matrix refinement based on F with *SHELX*76 minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/(\sigma^2 + 0{\cdot}001|F_o|^2)$ from counting statistics. H [calculated for C(9) and C(10)] riding with $U = 0{\cdot}05$ Å^2 on C atoms at 1·00 Å. Other H's from difference map refined positionally, isotropically. Reflections $\bar{2}12$, $\bar{4}32$, $1\bar{1}3$ (I) and 201 (II) given zero weight because they were affected badly by extinction. Refinement converged (I): $R = 0{\cdot}031$, $wR = 0{\cdot}041$, $S = 3{\cdot}10$, $|\Delta/\sigma|_{\max} = 0{\cdot}12$, $(\Delta\rho)_{\max}/(\Delta\rho)_{\min}$ 0·6/−0·6 e Å^{-3} and (II): $R = 0{\cdot}033$, $wR = 0{\cdot}049$, $S = 3{\cdot}51$, $|\Delta/\sigma|_{\max} = 0{\cdot}47$, $(\Delta\rho)_{\max}/(\Delta\rho)_{\min}$ 0·6/−0·7 e Å^{-3}. All 'large' peaks in final difference map around I and Br atoms. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1,* bond lengths and angles in Fig. 1.

Discussion. There is a disorder in both structures at the ethylene group C(9)–C(10), Fig. 1. This disorder is evident in many ET-based structures (Leung *et al.*, 1986; Psycharis *et al.*, 1988). The difference map shows two positions, *A* and *B*, for the ethylene group. The site occupancies for these two positions were refined, keeping the sum of the two constant at 1. They refined to 0·44 (I) and 0·70 (II) for positions *A*. This disorder is indicated in the illustration below.



In both structures the cations (donors) pack side by side in the plane of the molecule and we observe strong S···S interstack contacts (Fig. 2). Stacking is quite good (Fig. 3) and in (I) the intrastack contacts are weak (3·748 < S···S < 3·800 Å) but in (II) quite strong (3·468 < S···S < 3·695 Å) (Fig. 4).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44237 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

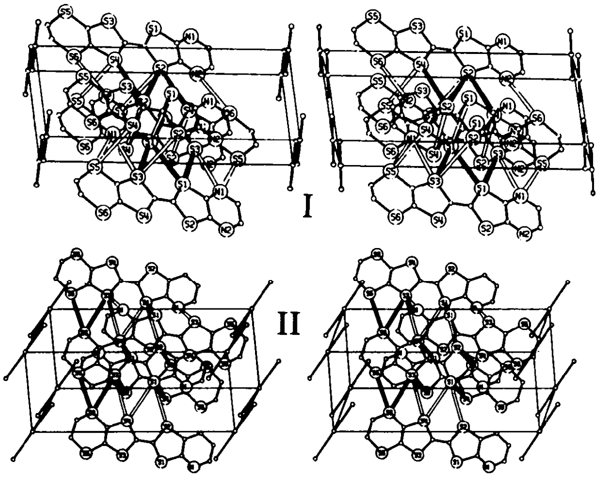
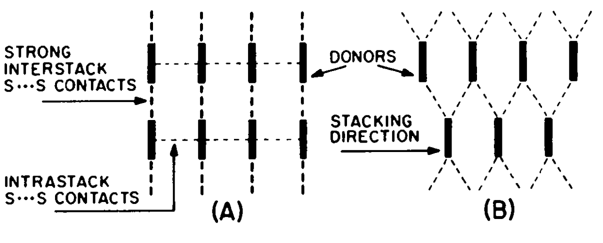


Fig. 4. Stereofigures looking down the *b* axis.

Although the donors (2)–(5) are *N*-modified molecules of the sulfur-based ET (1) their packing is very different from that of ET and more reminiscent of the selenium-based $(\mathrm{TMTSF})_2X$ salts (Williams & Carneiro, 1986). TMTSF molecules form stacks along the *a* crystallographic axis, which is also the direction of highest electrical conductivity, and the second 'dimensionality' arises from *inter*stack in-plane Se···Se contacts.

In the present cases, (3)–(5), the strong S···S contacts are in the plane of the donor (and this is expected to be the direction of highest conductivity) while the second 'dimensionality' is provided by weaker *intra*stack S···S contacts. In both cases, however, TMTSF and the present (3)–(5), the structures are made of donor 'sheet networks' separated by the anions. In $(\mathrm{ET})_2X$ ($X = \mathrm{I}_3^-$, IBr_2^-), quite differently, there are no intrastack S···S contacts and the second 'dimensionality' arises from bifurcated out-of-plane *inter*stack S···S contacts. To put it differently, in both TMTSF salts and the present (3)–(5), the stacks formed by the donors pack in phase and generate the 'sheet networks' (*A*), while in most ET salts they pack out of phase and generate the 'corrugated sheet network' (*B*).



Changes in the in-plane packing of the donors, that seem to be the result of the modifications on ET, are summarized in Fig. 5. In (2) the in-plane contacts are

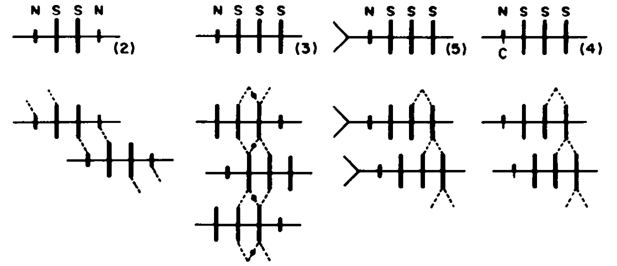


Fig. 5. Mode of in-plane packing of the various modifications of ET.

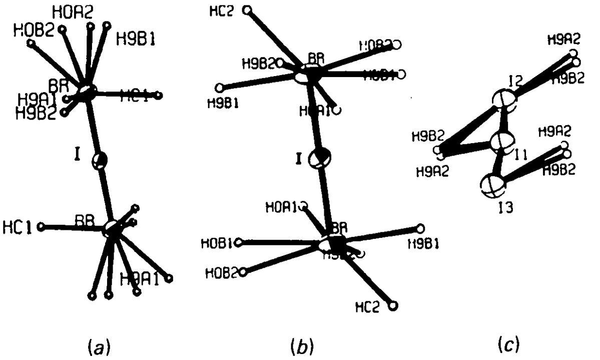


Fig. 6. The H-bonding environment of IBr_2^- and I_3^-: (*a*) refers to (I), (*b*) to (II); for (*c*) see text.

S···N and the second 'dimensionality' is provided by π–π interactions (Terzis *et al.*, 1986). In (3), (4) and (5) the in-plane contacts are strong S···S and the second 'dimensionality' is provided by weaker S···S contacts, but while in (3) the donors are related by a center of symmetry, in (4) and (5) they are related by translation. In going from (5) to (4) there seems to be an improvement in that while the strong in-plane S···S contacts are preserved there is a strengthening of the intrastack S···S contacts (S1···S1 = 3·468 Å) as well.

Anions. In the structures of (3) and (5) with I_3^- (Psycharis *et al.*, 1988) and (3) and (4) with IBr_2^- (present study) the overall packing is similar in that there are 'sheet networks' of donors separated by columns of anions. Yet in the I_3^- salts the anions are disordered while in the IBr_2^- salts they are ordered. The reason seems to lie in the mode of anion packing. In all four structures the anions occupy the cavities defined by the H atoms at each end of the donor molecules. In the I_3^- salts the anions pack head-to-tail in an almost straight line along the anion-column directions and any I···H contacts are on the side of the anion, Fig. 6(*c*), which is probably not conducive to pinning down the anions. In the IBr_2^- salts the anions, being smaller, are tilted from the anion-column direction towards the donor molecules and the Br···H contacts form caps at both ends of IBr_2^-, Fig. 6(*a*),(*b*), thus pinning down the anion.

AT thanks Bob Bau and the Chemistry Department of the University of Southern California for their hospitality and use of their facilities.

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Acta Cryst. (1988). C**44**, 132–135

The Structure of 2-Dimethylamino-6-oxo-4-phenyl-1,3-oxazin-5-carbaldehyde

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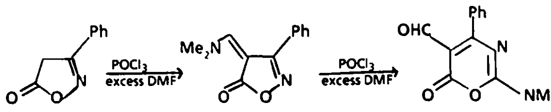
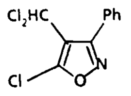
Abstract. $C_{13}H_{12}N_2O_3$, $M_r = 244{\cdot}25$, triclinic, $P\bar{1}$, $a = 8{\cdot}862\,(6)$, $b = 10{\cdot}041\,(2)$, $c = 14{\cdot}550\,(1)$ Å, $\alpha = 97{\cdot}00\,(1)$, $\beta = 83{\cdot}32\,(2)$, $\gamma = 116{\cdot}03\,(2)°$, $V = 1151{\cdot}8\,(13)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 7{\cdot}5$ cm^{-1}, $F(000) = 256$, $T = 123$ K, $R = 0{\cdot}054$ for 3773 unique reflections. The structure has an unusual number of close intermolecular contacts. The dense packing causes significant nonplanarity of the oxazine ring in one of the two symmetry-independent molecules, and causes disorder of the aldehyde O and H atoms in the other molecule.

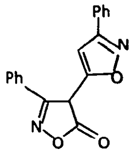
Introduction. Under Vilsmeier conditions, the title compound (3) is formed from 3-phenyl-5(4*H*)-isoxazolone (1) *via* (2) when it is reacted with $POCl_3$–excess *N,N*-dimethylformamide (DMF). This ring-expanded product was unexpected in the light of a literature report (Kallury & Devi, 1977) that the reaction products are a trichloroisoxazole (4) and a bis-adduct (5). Reactions of (1) with the same and modified conditions were then studied in detail, and mechanisms of the transformations were worked out (Anderson, 1986). In none of the reactions were (4) or (5) ever produced.



(1) (2) (3)



(4)



(5)

An X-ray crystallographic study of (3) was performed in order to confirm the structure beyond doubt.

Experimental. Clear chunky prism $0{\cdot}60 \times 0{\cdot}20 \times 0{\cdot}70$ mm; Nicolet $P\bar{1}$ diffractometer controlled by Harris computer; graphite monochromator, Cu $K\alpha$; $2\theta_{\max} = 138°$; all 3773 unique reflections measured, 3397 intensities $>2\sigma$; 2° min^{-1} $\theta/2\theta$ step scans, scan widths $>3{\cdot}4°$; 10 reflections periodically monitored showed no trend towards deterioration; $\sigma^2(I)$ was approximated by $\sigma^2(I)$ from counting statistics + $(0{\cdot}018I)^2$, where the coefficient of I was calculated from the variations in intensities of the monitored reflections; cell parameters by least-squares fit of Cu $K\alpha_1$ 2θ values [λ(Cu $K\alpha_1$) = $1{\cdot}5402$ Å] for 25 high-2θ reflections (Duchamp, 1977); Lp correction appropriate for a monochromator with 50% perfect character, no absorption correction. The structure was solved by direct methods, using *DIREC* (Duchamp, 1984*a*), H atoms were found in difference maps; except for methyl H atoms, generated positions were used. The aldehyde O and H atoms in the primed molecule are disordered; in a population of molecules, this substituent is rotated

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