

## Structure of the Red, Semiconducting Form of 4,4',5,5'-Tetramethyl- $\Delta^{2,2'}$ -bi-1,3-diselenole-7,7,8,8-Tetracyano-*p*-quinodimethane, TMTSF-TCNQ\*

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### Abstract

A red, semiconducting salt containing TMTSF and TCNQ crystallizes in the triclinic system, space group  $P\bar{1}$ , with one molecule of each component in a unit cell with the following crystal data:  $C_{10}H_{12}Se_4 \cdot C_{12}H_4N_4$ ,  $M_r = 652.24$ ,  $a = 8.096$  (3),  $b = 10.465$  (3),  $c = 6.998$  (2) Å,  $\alpha = 103.78$  (2),  $\beta = 98.49$  (3),  $\gamma = 94.91$  (3)°,  $V = 565.0$  (3) Å<sup>3</sup>,  $D_m = 1.94$  (1),  $D_c = 1.92$  g cm<sup>-3</sup>. Intensity data, collected by counter methods on an automated diffractometer operating in the  $\theta$ - $2\theta$  scan mode and employing monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å,  $\mu = 71.2$  cm<sup>-1</sup>), gave 2306 non-zero reflections which were used in the refinement of a standard heavy-atom solution by the full-matrix least-squares method. With fully anisotropic parameters for the nonhydrogen atoms and fixed, isotropic parameters for the H atoms, a final  $R$  value of 0.045 was obtained. The structure is composed of stacks of alternating TCNQ and TMTSF molecules positioned about centers of symmetry along the crystallographic  $c$  axis and separated by  $\sim 3.5$  Å. Each molecular component is rather planar and the TCNQ molecule is very nearly parallel to and directly centered above and below each adjacent TMTSF molecule and *vice versa*. The observed stacking pattern yields an excellent approximation to a mixed-stack array whose  $\pi$ -molecular charge-transfer integral is zero. It is estimated from vibrational frequency data and structural considerations that the degree of charge transfer is non-zero and approximately 0.2 e. The non-zero charge transfer is suggested to arise from the admixing of excited-state molecular orbitals within the mixed-stack crystal band.

### Introduction

The 1:1 salts of closed-shell organic electron donors with the acceptor TCNQ, 7,7,8,8-tetracyano-*p*-quino-

dimethane, or its analogs form crystal structures which typically fall into one of two broad categories (Herbststein, 1971). In the first, donor molecules ( $D$ ) and acceptor molecules ( $A$ ) alternate to form mixed stacks in the pattern  $\dots DADADADA \dots$ ; in the second, the molecules segregate so as to form parallel stacks of donors  $\dots DDDD \dots$  and acceptors  $\dots AAAA \dots$ . Electrically, materials of the first class are limited by simple band theory to semiconducting behavior, whereas the second type embraces a full range from insulators to metals whose conductivities often exceed  $10^4 \Omega^{-1} \text{cm}^{-1}$  at low temperatures. The basic factors underlying the relative stability of the two types of structures have remained a persistent puzzle, central to the systematics and design of organic conductors.

Of special interest in this context are the very few borderline compounds which crystallize in both types of structures. Among the members of the TTF-TCNQ family, such dimorphism is known only for the TCNQ salt of the donor TMTSF (4,4',5,5'-tetramethyl- $\Delta^{2,2'}$ -bi-1,3-diselenole; Bechgaard, Cowan & Bloch, 1974; Kistenmacher, Emge, Shu & Cowan, 1979). Elsewhere (Bechgaard, Kistenmacher, Bloch & Cowan, 1977), we have described the preparation of both 1:1 phases: a black metallic conductor whose crystal structure (Bechgaard *et al.*, 1977) consists, as expected, of segregated stacks, and a red semiconductor with a room-temperature resistivity orders of magnitude higher and an activation energy of 0.17 eV. The electrical and magnetic properties of the black, metallic form have been reported in detail (Bloch, Carruthers, Poehler & Cowan, 1977).

In this study, we report the determination of the crystal structure of the red, semiconducting form of TMTSF-TCNQ and confirm our suspicion (Bechgaard *et al.*, 1977) that it consists of mixed stacks of alternating donors and acceptors. By analysis of the intramolecular bond lengths and vibrational frequency of the cyano stretch of the TCNQ acceptor, we examine the degree of charge transfer in the red, semiconducting phase. Finally, we observe that the geometry of stacking in the red form implies a near cancellation of the overlap between the frontier molecular orbitals of donor and acceptor molecules and

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suggest that band structures in materials of this class may involve appreciable admixture of molecular excited states.

### Experimental

TMTSF-TCNQ was prepared according to the procedure of Bechgaard, Cowan & Bloch (1974) and dark-red crystals were grown from acetonitrile or ethyl acetate solutions at room temperature. The neutral-buoyancy method was used to measure the crystal density in a mixture of bromoform and carbon tetrachloride and indicated one formula unit per cell in a triclinic lattice; space group  $P\bar{1}$  was assumed. Complete crystal data for the Delaunay reduced cell are given in the *Abstract*.

The crystal used for data collection was a parallelepiped, having faces of dimensions: (100)-(100) 0.11 mm, (010)-(010) 0.07 mm, (001)-(001) 0.33 mm. Unit-cell dimensions and their associated standard deviations were obtained from a least-squares fit to the setting angles of 15 centered reflections measured on a Syntex  $P\bar{1}$  automated diffractometer. The 2618 reflections in the  $+h$  hemisphere to  $2\theta = 55^\circ$  were surveyed on the diffractometer employing graphite-monochromatized Mo  $K\alpha$  radiation and the  $\theta/2\theta$  scan mode. Individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning ( $2\theta$ ) ranged from 2–24° min<sup>-1</sup>. Three standards were monitored after every 100 reflections, and their intensities showed no unusual variation over the course of the experiment. The 2618 measured intensities were reduced to 2306 non-zero reflections which were used as the basis of the structural solution and refinement. Observational variances were based on counting statistics plus a term  $(pI)^2$ , where  $p$  was taken to be 0.03 representing the expected error proportional to the diffracted intensity (Busing & Levy, 1957). The intensities and their derived standard deviations were corrected for Lorentz, polarization and absorption effects [ $\mu(\text{Mo } K\alpha) = 71.2 \text{ cm}^{-1}$ , with maximum and minimum transmission factors of 0.62 and 0.34, respectively]. An approximate absolute scale was derived by the method of Wilson (1942).

Patterson and Fourier methods were employed to obtain positional parameters for the nonhydrogen atoms. The H atoms were located from a difference Fourier synthesis and their isotropic thermal parameters were set at 5.0 Å<sup>2</sup> for those on the TCNQ molecule and 7.0 Å<sup>2</sup> for those on the TMTSF molecule. Full-matrix least-squares refinement of anisotropic nonhydrogen atoms with the inclusion of fixed H atoms led to a final  $R$  value  $(\sum |F_o| - |F_c|) / (\sum |F_o|)$  of 0.045. The final weighted  $R$  value  $\{(\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$  and goodness of fit  $\{(\sum w|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})\}^{1/2}$ , where NO = 2306 observations

Table 1. Final non-hydrogen-atom parameters ( $\times 10^4$ )

	$x$	$y$	$z$	$U_{\text{eq}}$ (Å <sup>2</sup> )†
Se(1)	10018 (0.5)*	2700 (0.4)	4064 (0.7)	459 (2)
Se(2)	7072 (0.5)	4522 (0.4)	4352 (0.7)	468 (2)
N(1)	8517 (5)	378 (4)	7903 (7)	746 (25)
N(2)	4469 (5)	2825 (4)	8444 (7)	697 (23)
C(1)	7751 (5)	1889 (5)	3443 (6)	454 (22)
C(2)	6520 (5)	2664 (4)	3566 (6)	467 (23)
C(3)	9436 (5)	4468 (3)	4708 (6)	391 (18)
C(4)	4649 (6)	2177 (5)	3160 (8)	701 (29)
C(5)	7516 (6)	410 (4)	2822 (8)	665 (27)
C(6)	5890 (6)	2795 (4)	8591 (7)	519 (26)
C(7)	8150 (5)	1426 (4)	8285 (7)	535 (23)
C(8)	7662 (5)	2727 (4)	8765 (6)	468 (23)
C(9)	8819 (5)	3848 (4)	9368 (6)	439 (22)
C(10)	8280 (5)	5142 (4)	9843 (6)	453 (23)
C(11)	10597 (5)	3756 (4)	9546 (6)	482 (25)

\* Estimated standard deviations in the least significant figure are enclosed in parentheses.

† The definition of  $U_{\text{eq}}$  is that of Willis & Pryor (1975).

and NV = 136 variables} were 0.037 and 1.6, respectively. The quantity minimized in the least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 4F_o^2/\sigma^2(F_o^2)$ . A final difference Fourier map was essentially featureless, with residual density peaks between  $\pm 0.95 \text{ e } \text{Å}^{-3}$  (near the Se-atom positions).

Neutral scattering factors for the nonhydrogen atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964), while those for the H atoms were from Stewart, Davidson & Simpson (1965). The scattering curves for all nonhydrogen atoms were corrected for anomalous-dispersion effects (Cromer & Liberman, 1970). Final atomic positional parameters for the nonhydrogen atoms are collected in Table 1.\*

Least-squares and structure factor calculations were carried out with a modified version of *ORFLS* (Busing, Martin & Levy, 1962); Fourier syntheses were computed with *FORDAP* (Zalkin, 1965); the absorption correction was applied using *ORABS* (Wehe, Busing & Levy, 1962); best planes were computed with *MEAN PLANE* (Pippy & Ahmed, 1968); illustrations were prepared with the aid of *ORTEP* (Johnson, 1965). Calculations not cited were performed with locally written programs.

## Results and discussion

### Crystal structure and intrastack interactions

The crystal packing of the red, semiconducting form of TMTSF-TCNQ is dominated by stacks of nearly

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36475 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parallel and alternating TMTSF and TCNQ molecules (see Fig. 1) with an intrastack molecular overlap pattern as displayed in Fig. 2. The angle between plane normals for the two molecular species ranges from 1.5–1.7° depending on which molecular plane is used to describe the TMTSF molecule (see Table 2). The mean separation between the slightly nonparallel molecular constituents is 3.5 Å (approximately  $c/2$ ); this magnitude of intermolecular separation is typical of mixed-stack systems with neutral or slightly ionic ground states (Herbstein, 1971). The red form of TMTSF–TCNQ is to our knowledge the first 1:1 charge-transfer salt derived from a heterofulvalene donor and a TCNQ acceptor which crystallizes, apparently with equal facility, in either a mixed-stack or a segregated-stack motif.

The pattern of molecular overlap depicted in Fig. 2 is remarkable from the point of view of orbital symmetry. The nominal symmetries of the highest occupied molecular orbitals of fractionally ionized TMTSF and TCNQ in the  $D_{2h}$  point group are  $b_{1u}$  and  $b_{2g}$ , respectively. In the stacking pattern of Fig. 2 the overlap between orbitals with these symmetries precisely cancels. Hence, to the extent that these sym-

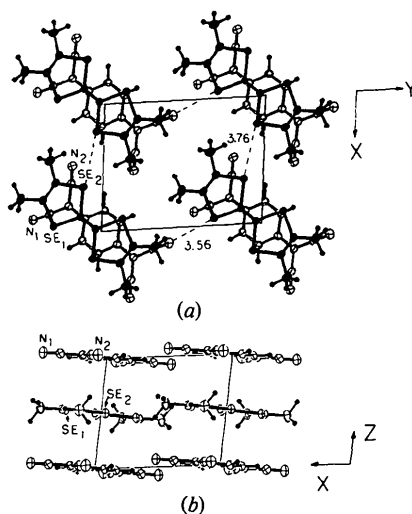


Fig. 1. Crystal packing in the red form of TMTSF–TCNQ as viewed along (a) the  $c^*$  axis and (b) the  $b^*$  axis.

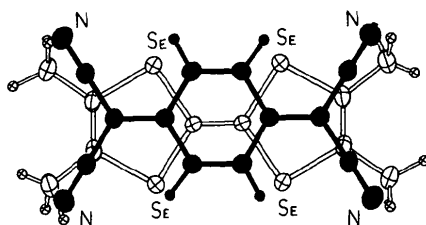


Fig. 2. The molecular overlap in columns of alternating donors and acceptors. The view direction is normal to the mean molecular plane of the TCNQ acceptor.

Table 2. *Some least-squares planes and deviations (Å) of individual atoms from these planes*

In each of the equations of the planes,  $X$ ,  $Y$ , and  $Z$  are coordinates (Å) referred to the orthogonal axes  $X$  along  $a$ ,  $Y$  in the  $ab$  plane and  $Z$  along  $c^*$ . Atoms indicated by a dagger were given zero weight in calculating the plane; all other atoms were equally weighted.

(a) TCNQ molecular plane ( $0.1026X + 0.2883Y - 0.9520Z = -4.6984$  Å)

N(1)	$\mp 0.005$ (5)	C(8)	$\pm 0.006$ (5)
N(2)	$\mp 0.006$ (5)	C(9)	$\pm 0.008$ (5)
C(6)	$\pm 0.000$ (6)	C(10)	$\pm 0.008$ (5)
C(7)	$\pm 0.003$ (6)	C(11)	$\pm 0.004$ (5)

(b) TMTSF planes

(1) TMTSF interior plane ( $0.1331X + 0.2846Y - 0.9494Z = -0.9953$  Å)

Se(1)	$\pm 0.002$ (1)	C(3)	$\mp 0.008$ (5)
Se(2)	$\pm 0.002$ (1)		

(2) TMTSF central plane ( $0.1273X + 0.2775Y - 0.9523Z = -1.0768$  Å)

Se(1)	$\pm 0.017$ (1)	C(2)	$\mp 0.010$ (5)
Se(2)	$\pm 0.019$ (1)	C(3)	$\mp 0.002$ (5)
C(1)	$\mp 0.007$ (5)	†C(4)	$\mp 0.049$ (6)
		†C(5)	$\mp 0.008$ (6)

(3) TMTSF exterior plane ( $0.1180X + 0.2650Y - 0.9570Z = -1.1668$  Å)

Se(1)	$-0.001$ (1)	C(1)	$+0.002$ (5)
Se(2)	$+0.001$ (1)	C(2)	$-0.002$ (5)

metries are pure, the width of the semiconducting valence band would vanish.

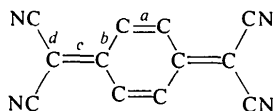
The achievement of a nominally zero-bandwidth *DA*-stacked semiconductor is interesting in two respects. First, the existence of such a material violates the criteria proposed by Metzger, Torrance, Mayerle & Crowley (1978), who argued that stacking should always occur in such a manner as to *maximize* frontier orbital overlap. Second, if the valence bandwidth is really zero, then the transfer of charge from the donor to the acceptor cannot be fractional: it must be identically either zero or unity (see, for example, McConnell, Hoffman & Metzger, 1965). Determination of the charge transfer in red TMTSF–TCNQ is then of special interest.

#### *Molecular geometry of the TCNQ molecule in red TMTSF–TCNQ and an estimate of the degree of charge transfer*

The interatomic bond lengths and angles in the quite planar (see Table 2) TCNQ molecule are displayed in Fig. 3 and compared to the molecular geometries of several other TCNQ species in Table 3. Both theory [see, for example, Haddon (1975) and Johanson (1975)] and experiment (Hoekstra, Spoelder & Vos, 1972) indicate a significant shift from a quinonoid to a

Table 3. TCNQ molecular geometry and estimated charge transfer

(a) Comparison of average bond lengths (Å) on TCNQ<sup>0</sup> and several of its charge-transfer salts (*mmm* molecular symmetry imposed)



	TCNQ <sup>0</sup> ( <sup>11</sup> )	Phenazine-TCNQ( <sup>2</sup> )	DPDO-TCNQ( <sup>13</sup> )	TMTSF-TCNQ( <sup>4</sup> ) (red)
<i>a</i>	1.346 (3)	1.340 (4)	1.344 (5)	1.354 (6)
<i>b</i>	1.448 (4)	1.436 (5)	1.430 (5)	1.438 (6)
<i>c</i>	1.374 (3)	1.364 (4)	1.361 (5)	1.375 (6)
<i>d</i>	1.441 (3)	1.437 (5)	1.432 (5)	1.429 (6)
	DMPH-TCNQ( <sup>5</sup> )	TMTSF-TCNQ( <sup>6</sup> ) (black)	TMPD(TCNQ) <sub>2</sub> ( <sup>7</sup> )	TMTSF-DMTCNQ( <sup>8</sup> )
<i>a</i>	1.351 (6)	1.39 (1)	1.353 (2)	1.360 (6)
<i>b</i>	1.430 (5)	1.44 (1)	1.431 (2)	1.441 (6)
<i>c</i>	1.383 (7)	1.39 (1)	1.394 (2)	1.398 (6)
<i>d</i>	1.436 (6)	1.42 (1)	1.423 (3)	1.423 (6)
	HMTTF-TCNQ( <sup>9</sup> )	TTF-TCNQ( <sup>10</sup> )	TMTTF-TCNQ( <sup>11</sup> )	TCNQ <sup>-</sup> ( <sup>12</sup> )
<i>a</i>	1.356 (4)	1.356 (3)	1.34 (1)	1.373 (4)
<i>b</i>	1.434 (4)	1.433 (3)	1.44 (1)	1.423 (4)
<i>c</i>	1.397 (4)	1.402 (3)	1.41 (1)	1.420 (4)
<i>d</i>	1.421 (4)	1.423 (3)	1.42 (1)	1.416 (4)

(b) Predicted charge transfer (CT) based on TCNQ dimensions

	<i>c</i> /( <i>b</i> + <i>d</i> )	Predicted CT	Experimental CT
TCNQ <sup>0</sup> ( <sup>11</sup> )	0.476	0.00 e	0.0 e
Phenazine-TCNQ( <sup>2</sup> )	0.475	0.00	—
DPDO-TCNQ( <sup>13</sup> )	0.476	0.00	—
TMTSF-TCNQ (red)( <sup>4</sup> )	0.480	0.17	0.21( <sup>13</sup> )
DMPH-TCNQ( <sup>5</sup> )	0.483	0.29	—
TMTSF-TCNQ (black)( <sup>6</sup> )	0.486	0.42	0.57( <sup>13</sup> ), 0.61( <sup>18</sup> )
TMPD(TCNQ) <sub>2</sub> ( <sup>7</sup> )	0.488	0.50	0.50( <sup>14</sup> )
TMTSF-DMTCNQ( <sup>8</sup> )	0.488	0.50	0.50( <sup>15</sup> )
HMTTF-TCNQ( <sup>9</sup> )	0.489	0.54	0.72( <sup>13</sup> ), 0.72( <sup>16</sup> )
TTF-TCNQ( <sup>10</sup> )	0.491	0.62	0.59( <sup>13</sup> ), 0.59( <sup>17</sup> )
TMTTF-TCNQ( <sup>11</sup> )	0.493	0.71	—
TCNQ <sup>-</sup> ( <sup>12</sup> )	0.500	1.00	1.00

References: (1) Long, Sparks & Trueblood (1965); (2) Goldberg & Shmueli (1973c); (3) Goldberg & Shmueli (1973b); (4) this work; (5) Goldberg & Shmueli (1973a); (6) Bechgaard *et al.* (1977); (7) Hanson (1968); (8) Andersen *et al.* (1978); (9) Chasseau, Comberton, Gaultier & Hauw (1978); (10) Kistenmacher *et al.* (1974); (11) Phillips, Kistenmacher, Cowan, Bechgaard & Bloch (1977); (12) Hoekstra *et al.* (1972) for Rb<sup>+</sup>.TCNQ<sup>-</sup>; (13) Chappell *et al.* (1981); (14) assumed from stoichiometry; (15) Andrieux, Duroure, Jérôme & Bechgaard (1979); (16) Megtert, Pouget & Comès (1978); (17) Denoyer, Comès, Garito & Heeger (1975), Kagoshima, Anzai, Kajimura & Ishiguro (1975), Pouget, Khanna, Denoyer, Comès, Garito & Heeger (1976), Coppens & Row (1978); (18) Pouget (1980).

benzenoid structure for the TCNQ molecule with increasing charge. The very close similarity between the molecular dimensions for TCNQ<sup>0</sup> (Long, Sparks & Trueblood, 1965) and those for the TCNQ molecule in red TMTSF-TCNQ suggests a low degree of charge transfer in this system.

Recently, two empirical schemes (Coppens & Row, 1978; Flandrois & Chasseau, 1977) have been put forward for estimating the degree of charge transfer based on TCNQ geometry, reasoning from the nodal structure of the frontier *b*<sub>2g</sub> molecular orbital. Both schemes focus on the lengthening of the formal double bonds *a* and *c* and the shortening of the formal single bonds *b* and *d* (Table 3) as the structure becomes more benzenoid in character with increasing charge. We reason in the same spirit, but propose here a slightly different scheme. In comparing the TCNQ-containing species in Table 3, we estimate the degree of charge transfer based on the ratio *c*/(*b* + *d*). We expect this to be a better index of charge transfer than the previous schemes because of the concentration of spin density (see, for example, Jonkman, Van Der Velde & Nieuwpoort, 1974) in the vicinity of *c* rather than *a*. In general the agreement between the charge transfer estimated in this way and the charge transfer based on other physical properties of these compounds is quite satisfying, Table 3.

The result of this analysis is an effective charge on the TCNQ acceptor in red TMTSF-TCNQ of -0.17 e, a value which is small but significantly different from zero. Our conclusion is buttressed by the spectroscopic results of Chappell, Bloch, Bryden, Maxfield, Poehler & Cowan (1981), who, based on the cyano stretching frequency of the TCNQ molecule, derive a value of -0.21 e. It follows from the discussion of the previous section that finite charge transfer can arise in the present structure only if the intermolecular banding involves a strong admixture of molecular excited states, such as the low-lying TMTSF states of *g* symmetry. To

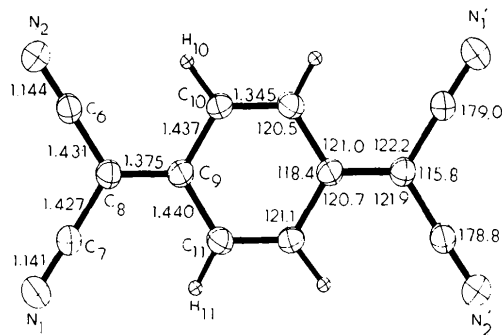


Fig. 3. The TCNQ molecule viewed normal to its mean plane. The thermal ellipsoids of the nonhydrogen atoms are drawn at the 30% probability level. The isotropic thermal parameters for the H atoms have been artificially set to 1.0 Å<sup>2</sup>. Estimated standard deviations for nonhydrogen-atom bond lengths are approximately 0.006 Å; bond angles are within 0.3–0.4°.



These interactions are primarily of two types:  $\text{Se} \cdots \text{Se}$  and  $\text{Se} \cdots \text{N}$ . Along the crystallographic  $a$  axis, there is a significant  $\text{Se}(2) \cdots \text{Se}(2; 1-x, -y, -z)$  contact at 3.758 (1) Å, which is perhaps one of the strongest interstack interactions in this structure [but still near the expected van der Waals separation of about 3.9 Å and similar to contacts found in several conducting complexes (Kistenmacher, 1978)]. Along the crystallographic  $b$  axis, the interchain coupling is dominated by an  $\text{Se}(1) \cdots \text{N}(1; -x, 1-y, -z)$  contact at 3.564 (4) Å, again at an expected van der Waals separation. For the black form, interstack interactions of this  $\text{Se} \cdots \text{Se}$  type are at 3.98 (1) Å, and at 3.36 (1) Å for the  $\text{Se} \cdots \text{N}$  type, with the  $\text{Se} \cdots \text{Se}$  distance elongated and the  $\text{Se} \cdots \text{N}$  distance contracted in the more ionic black form as expected. Contacts involving the exocyclic methyl groups of the TMTSF molecule and other atoms are also at or near to their expected van der Waals separations; *i.e.*  $\text{N}(1) \cdots \text{C}(4; 1-x, 1-y, -z) = 3.404$  (6) and  $\text{C}(4) \cdots \text{C}(5; 1-x, 1-y, 1-z) = 4.021$  (7) Å.

### Summary

The structure of red TMTSF-TCNQ provides a unique example of a 1:1 heterofulvalene salt with TCNQ in a mixed-stack, columnar motif. The parallelism of the donor and acceptor molecules, which was previously thought to yield only complexes with slipped, segregated stacks, as in the black conducting polymorph of TMTSF-TCNQ, here gives a mixed stack where donors are situated directly above acceptors and *vice versa*. The near cancellation of nearest-neighbor  $\pi$ -molecular-orbital overlap produces an interesting system of TMTSF and TCNQ molecules whose states are predicted by simple theory to be either neutral or fully ionic. The charge transfer in red TMTSF-TCNQ is believed to be  $\sim 0.2 e$  from experiment and to arise from admixing of excited-state molecular orbitals, predominantly donor in character, within the mixed-stack crystal band. Since this charge-transfer complex exists near a zero-bandwidth limit, studies underway concerning its optical and magnetic properties should prove to be of special interest.

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## Structure du *p*-Bromobenzoylglycinate de Hydroxy-2 Cyclopentyle-*trans*

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### Abstract

Crystals of  $C_{14}H_{16}BrNO_4$  are monoclinic, space group  $C2/c$ ,  $a = 28.38$  (4),  $b = 9.18$  (1),  $c = 12.349$  (2) Å,  $\beta = 108.76$  (4)°,  $Z = 8$ ,  $V = 3046$  (8) Å<sup>3</sup>,  $d_m = 1.49$ ,  $d_c = 1.51$  Mg m<sup>-3</sup>,  $M_r = 342.19$ . X-ray diffraction intensity data for 1655 observed reflexions were recorded at room temperature with an automated diffractometer. The structure was determined by the heavy-atom method and refined by full-matrix least squares to  $R = 0.06$ . The oxygen of the hydroxyl group does not form an intramolecular hydrogen bond with the carbonyl oxygen of the ester function, but is involved in two intermolecular hydrogen bonds. The hydroxyl group acts as a donor through its hydrogen to the oxygen of the peptide group of a second molecule and as an acceptor through the hydrogen of the peptidic nitrogen from a third molecule so building infinite chains.

### Introduction

La synthèse du *p*-bromobenzoylglycinate de hydroxy-2 cyclopentyle-*trans* a été réalisée par Mestdagh & Julia

(communication personnelle). Il est intéressant de savoir si, dans un hydroxyester de ce type, l'un des oxygènes du groupement ester participe à une liaison hydrogène: la réactivité du groupement carbonyle pourrait s'en trouver modifiée.

La forme *trans* fut obtenue en faisant en premier lieu la synthèse de la *p*-bromobenzoylglycine puis celle du fluoborate de *p*-bromophényl-2 oxazolonium. Une solution de cette substance dans l'acétonitrile anhydre était alors ajoutée à une solution de cyclopentanediol-*trans* dans de l'acétonitrile anhydre. Après extraction, la phase organique était lavée et séchée. Le monoester était ensuite séparé par chromatographie. Deux cristallisations dans l'éther ont fourni les cristaux permettant une étude aux rayons X ( $T_f = 365$  K). Ils se présentent sous forme de prismes plus ou moins allongés, le plus souvent d'un blanc opaque mais les plus petits sont transparents et s'éteignent parfaitement au microscope polarisant. Ils appartiennent au système monoclinique avec comme groupe spatial  $C2/c$ .

La structure a été établie à partir des données d'un diffractomètre automatique CAD-3 Enraf-Nonius avec anticathode de cuivre et filtre de nickel, en utilisant un cristal ayant comme dimensions: 0,15 × 0,21 × 0,37 mm. Les intensités furent enregistrées à la