Acta Cryst. (1981). B37, 2030–2034

Segregated Stacking in Organic Charge-Transfer Complexes: Tetramethyltetrathiafulvalene (TMTTF)–Bromanil*

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(*Received* 1 *December* 1980; *accepted* 6 *April* 1981)

Abstract

TMTTF–bromanil is the first 1:1 organic charge-transfer compound found to crystallize in segregated stacks of donors and acceptors that does not contain tetracyano-*p*-quinodimethane (TCNQ) or a TCNQ-like molecule as the acceptor. TMTTF–bromanil, $C_{10}H_{12}S_4.C_6Br_4O_2$, M_r = 684·12, crystallizes in the monoclinic space group $C2/c$ with a = 31·316 (7), b = 3·9499 (7), c = 19·300 (4) Å, β = 121·19 (2)°, Z = 4, D_c = 2·22, D_o = 2·21 (2) Mg m^{-3}. Final R = 0·042 for 1308 observed reflections. A detailed comparison of the structure of TMTTF–bromanil to that of TMTTF–TCNQ reveals striking similarities. Both highly conducting materials consist of segregated stacks of evenly spaced donor and acceptor molecules. The intermolecular overlaps of neighboring TMTTF molecules within a stack are virtually identical while the acceptor–acceptor overlaps in both structures are of the 'ring–exocyclic double-bond' type found in all highly conducting TCNQ salts. The main difference in the two structures is the interplanar spacing between the acceptor molecules. This distance is 3·27 Å in TMTTF–TCNQ and 3·39 Å in TMTTF–bromanil. This large separation, caused by the bulk of the Br atoms, is presumably related to the poorer conductivity of the bromanil salt.

Introduction

Of all the organic charge-transfer complexes known, the overwhelming majority crystallize such that the donor and acceptor molecules lie alternately one over the other in infinite columns. Only a very few crystallize with separate (segregated) stacks of donors and acceptors. This latter packing mode is one of the prerequisites for high electrical conductivity in these types of materials. Until recently, however, the only 1:1 charge-transfer salts in which segregated stacking was found were those materials in which tetracyano-*p*-quinodimethane (TCNQ) or a derivative thereof was the acceptor molecule. We recently reported (Torrance, Mayerle, Lee & Bechgaard, 1979) the discovery of a new class of highly conducting 1:1 charge-transfer salts, those formed between tetrathiafulvalene (TTF) and its derivatives with the tetrahalo-*p*-benzoquinones. More recently, we have reported (Mayerle & Torrance, 1980*a*) the properties of the TTF and dibenzo-TTF salts of dichlorodicyano-*p*-benzoquinone. These are the first examples of materials not containing TCNQ-like molecules to crystallize in segregated stacks. We present here a complete structural analysis of one of those salts, that formed by tetramethyltetrathiafulvalene and tetrabromo-*p*-benzoquinone (TMTTF–bromanil, hereafter TMTTF–brl), and make a detailed comparison between it and its TCNQ counterpart, TMTTF–TCNQ.

Experimental

TMTTF–brl was prepared by the reaction of stoichiometric quantities of the constituent molecules in acetonitrile. On rare occasions, cooling of the reaction solution led to crystals of useful size and quality. The crystal used for data collection was an eight-sided needle 0·16 mm thick and 0·32 mm long. The sides of the needle were defined by faces of the form (100), (10$\bar{1}$), (20$\bar{1}$) and (001). The ends of the needle were capped by the (010) faces. The crystal was mounted on the end of a glass fiber and transferred to an Enraf–Nonius CAD-4 diffractometer. Following machine location of 20 reflections, a preliminary triclinic unit cell and orientation matrix were computed. A Delaunay reduction showed the cell to be C-centered monoclinic rather than triclinic and the cell was transformed accordingly. The final unit-cell parameters were obtained by a least-squares fitting to the setting angles of 15 high-angle ($2\theta > 32°$) reflections, based on graphite-monochromatized Mo $K\alpha_1$ radiation (λ = 0·70930 Å).

Several open-counter ω scans gave peak widths at half-height of 0·2–0·25°. Data ($\pm h,k,l$) were collected

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* Bromanil is 2,3,5,6-tetrabromo-*p*-benzoquinone.

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by the θ–2θ scan method to $\theta = 30°$. Graphite-monochromatized Mo $K\alpha$ radiation was used. The scan range was computed according to the equation $\Delta\theta = (1{\cdot}0 + 0{\cdot}35 \tan\theta)°$ and was extended by 25% on each end of the scan for background measurement. The scan rate varied between 1·3 and 10° min^{-1} based upon the intensity of a fast prescan. An aperture with a height of 4 mm and a variable width of $(3{\cdot}0 + 2{\cdot}11 \tan\theta)$ mm was placed in front of the scintillation counter at a distance of 173 mm from the crystal. The intensities of three standard reflections, measured after every 100 min of X-ray exposure, varied by no more than 2% about their mean over the course of data collection. A total of 2014 reflections were collected, 1308 of which were judged to be observed by the criterion $F_o^2 \geq 2\sigma(F_o^2)$. The data were corrected for Lp and absorption effects. The transmission factors ranged between 0·235 and 0·352 based on a linear absorption coefficient of 8·81 mm^{-1}.

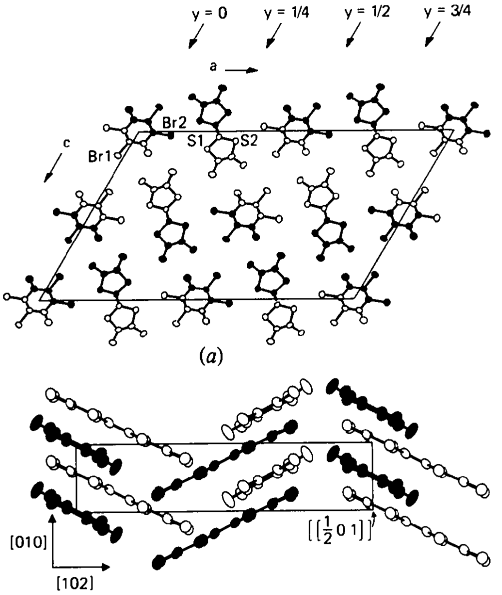
The coordinates of the atoms in $C2/c$ were obtained by transformation of the coordinates originally obtained by solution in the triclinic space group $P\bar{1}$. For that solution the x and z coordinates of all the atoms were obtained by graphical techniques. These were used to solve the Patterson map for the y coordinate of the Br and S atoms. Subsequent difference Fourier syntheses revealed the remainder of the structure. Anisotropic refinement of all non-H atoms converged at $R = 0{\cdot}042$ and $R_w = 0{\cdot}046$ based on 118 variables and 1308 reflections and using as weights $w = 4F_o^2/\sigma^2(F_o^2)$. During the last cycle of refinement no parameter changed by more than 0·004 that of its standard deviation. A difference map computed after the final cycle of refinement showed some electron density near the methyl C atoms. However, most of the peaks were in unreasonable positions, so no further refinement was carried out. The neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, pp. 72–98), as were the corrections for anomalous dispersion applied to the scattering factors of S and Br (*International Tables*, 1974, pp. 149–150). Computations were performed on an IBM 370/168 computer with programs described previously (Mayerle, 1977). The final atomic positional parameters are listed in Table 1.*

Table 1. *Final atomic positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq} (Å^2)
Br(1)	−198·8 (3)	−2486 (3)	1431·5 (5)	44·5 (4)
Br(2)	1105·1 (3)	−1411 (2)	248·2 (5)	45·6 (5)
S(1)	2512·1 (7)	724 (6)	1081 (1)	57 (2)
S(2)	3258·1 (7)	495 (6)	610 (1)	50 (2)
O	707 (2)	−3352 (17)	1296 (3)	63 (4)
C(1)	3088 (3)	−983 (21)	1787 (4)	39 (5)
C(2)	3432 (3)	−1164 (20)	1563 (4)	36 (5)
C(3)	2659 (2)	1712 (20)	354 (4)	32 (4)
C(4)	3156 (3)	−2199 (23)	2582 (5)	48 (5)
C(5)	3958 (3)	−2545 (24)	2046 (4)	45 (5)
C(6)	−115 (3)	−1028 (21)	586 (4)	36 (4)
C(7)	381 (3)	−1819 (23)	706 (4)	41 (4)
C(8)	470 (3)	−500 (20)	66 (4)	36 (4)

Discussion

TMTTF–brl is an important member of a new class of organic charge-transfer solids formed by the donors TTF and TMTTF with the tetrahalo-*p*-benzoquinones as acceptors. These materials were chosen for study because they were expected to have a high probability of forming segregated stacks and of being mixed valence, two conditions (Torrance, 1979; Mayerle, 1980) that must be met to achieve high conductivity in this type of material. This expectation was based on their mutually favorable molecular-orbital symmetry and solution redox potentials, as discussed previously (Torrance *et al.*, 1979). We have found that the 1:1 compounds in this class of materials give rise to several phases, some of which, as indicated by their high conductivity, have segregated stacks. Obtaining single crystals of the highly conducting phases proved to be



(*a*)

(*b*)

Fig. 1. (*a*) The (010) projection of TMTTF–bromanil. The y coordinates of the chains of stacks are given at the top. (*b*) The crystal packing in the $(20\bar{1})$ plane of TMTTF–bromanil.

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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 36150 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

extremely difficult. Apart from TMTTF–brl, the structure of which is reported here, we have been able to obtain single crystals of phases with only mixed stacks (Mayerle, Torrance & Crowley, 1979).

TMTTF–brl crystallizes in at least two phases of 1:1 stoichiometry. The structure we report here is of the highly conducting phase, which crystallizes in separate (segregated) stacks of *evenly* spaced donor and acceptor molecules. The (010) and (20$\bar{1}$) projections of the structure are shown in Figs. 1(*a*) and 1(*b*) respectively. Both donor and acceptor lie on inversion centers and are therefore required to have $\bar{1}$ molecular symmetry. The molecular geometries of the TMTTF cation and bromanil anion are illustrated in Figs. 3 and 4 respectively. E.s.d.'s for the various bond lengths and angles are: S–C 0·007, Br–C 0·007, C–O 0·009, C–C 0·010 Å; angles, 0·5–0·7°. Both donor and acceptor are essentially planar, the former to within 0·02 Å for all atoms and the latter to within 0·04 Å.

In general, one might expect the degree of charge transfer to affect the molecular geometry of the donor and acceptor molecules. Comparison of the dimensions of the TTF molecule in various structures, however, reveals no clear systematic correlations. We cannot, therefore, deduce an independent estimate of the degree of charge transfer from the geometry of TMTTF (Fig. 3), although we can point out that the molecular dimensions of the TMTTF molecules in TMTTF–brl and TMTTF–TCNQ (Phillips, Kistenmacher, Bloch, Ferraris & Cowan, 1976) are identical within experimental error. Spectroscopic methods have determined the degree of charge transfer (ρ) to be $0{\cdot}5 \leq \rho \leq 0{\cdot}6$ for TMTTF–brl (Torrance, Mayerle, Lee, Bozio & Pecile, 1981).

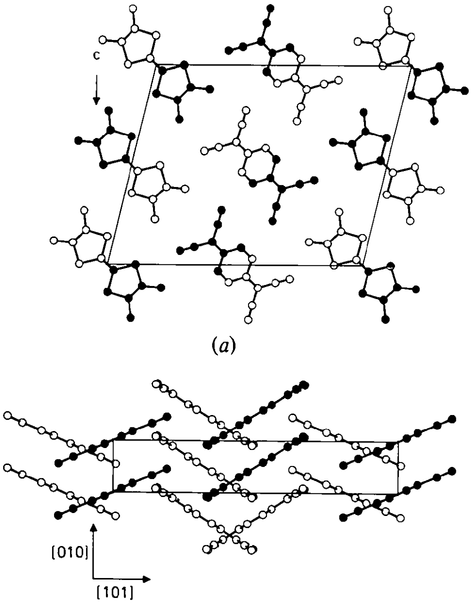

Fig. 2. (*a*) The (101) projection of TMTTF–TCNQ. (*b*) The crystal packing in the (10$\bar{1}$) plane of TMTTF–TCNQ (Phillips *et al.*, 1976).

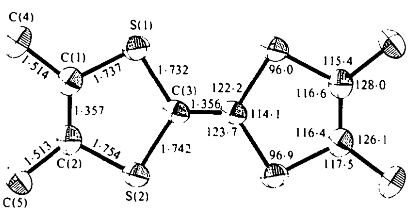

Fig. 3. The molecular dimensions of the TMTTF molecule.

A comparison of the geometric parameters of the bromanil molecules to that of the bromanil molecule in other structures is somewhat interesting. Since the lowest unoccupied molecular orbital (LUMO) of bromanil is bonding with respect to bonds C(6)–C(7) and C(7)–C(8) and antibonding with respect to bonds C(7)–O and C(6)–C(8) (Metzger, 1978, by analogy to chloranil), the first two would be expected to be shorter in the anion than in the neutral molecule while the latter two would be expected to be longer. Indeed the C(6)–C(7) bond decreases in length from 1·484 (12) Å in neutral bromanil (Crowley, 1980) to 1·444 (8) Å in ionic TTF–brl (Mayerle & Torrance, 1980*b*, unpublished results). Although barely significant statistically, the change is in the right direction. Also, as expected, the C(6)–C(8) and C(7)–O bond lengths increase from 1·318 (9) and 1·215 (9) Å to 1·358 (8) and 1·245 (7) Å respectively, upon reduction. It is interesting, therefore, to observe that the multiple bond lengths of the bromanil molecule in TMTTF–bromanil are virtually the same as they are in neutral bromanil and distinctly different from those in ionic TTF–brl. Thus, although optical data show the material to be mixed valence and Raman data indicate the degree of charge transfer to be ~0·6 (Torrance *et al.*, 1981), only the dimensions of the TMTTF molecule are consistent with this. We do not understand the discrepancy for the bromanil molecule.

Most interesting, and probably the most important in terms of physical properties, is a comparison of the relative arrangement of molecules within the stacks. The molecular overlaps in the donor and acceptor columns are shown in Figs. 5 and 6 respectively. For com-

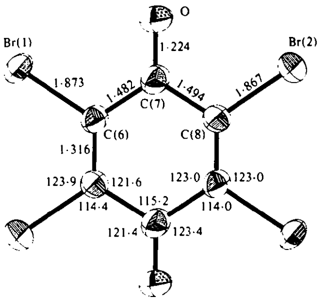

Fig. 4. The molecular dimensions of the bromanil molecule.

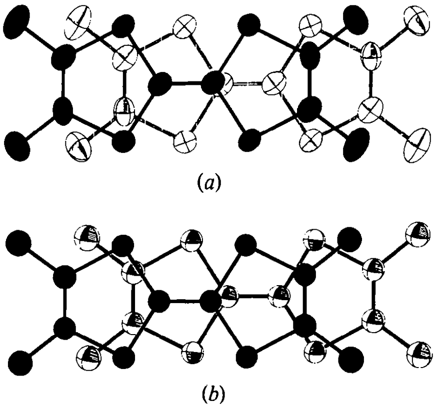

Fig. 5. (*a*) The TMTTF overlap in TMTTF–bromanil. The interplanar spacing is 3·54 Å. (*b*) The TMTTF overlap in TMTTF–TCNQ. The interplanar spacing is 3·53 Å (Phillips *et al.*, 1976).

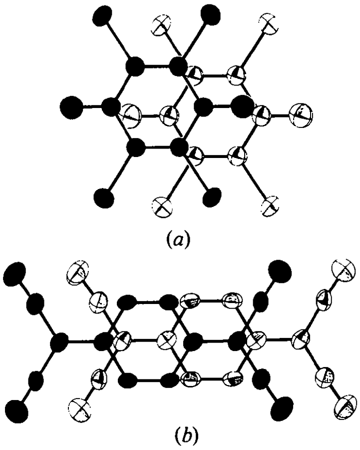

Fig. 6. (*a*) The bromanil overlap in TMTTF–bromanil. The interplanar spacing is 3·38 Å. (*b*) The TCNQ overlap in TMTTF–TCNQ. The interplanar spacing is 3·27 Å (Phillips *et al.*, 1976). The overlap is of the ring–exocyclic double-bond type in both structures.

parative purposes the overlaps in the donor and acceptor stacks of TMTTF–TCNQ (Phillips *et al.*, 1976) are included. As can be seen in Fig. 5, the overlap of the TMTTF molecules is virtually identical in the two structures. So, too, are the interplanar spacings of the TMTTF molecules: 3·54 Å in TMTTF–brl and 3·53 Å in TMTTF–TCNQ.

Although the acceptor molecules in the two structures are quite different sterically, they both have a quinoid electronic structure and a comparison of the molecular overlaps shows just how similar the two structures are. Fig. 6(*b*) illustrates the TCNQ overlap in TMTTF–TCNQ. As in all the highly conducting TCNQ salts examined to date, the overlap is of the 'ring–exocyclic double-bond' type, *i.e.* the exocyclic C=C double bond lies over the quinoid ring of the molecule adjacent to it in the same stack (Fig. 6*b*). The average interplanar spacing between the TCNQ molecules is 3·27 Å and the normal to the molecular planes makes an angle of 31·9° with respect to the stacking axis. As shown in Fig. 6(*a*), the bromanil molecules in TMTTF–brl stack such that the exocyclic C=O double bond of one molecule lies over the quinoid ring of its neighboring molecule. Thus, although the bromanil and TCNQ molecules are grossly different, their molecular overlaps are quite analogous to each other. This slippage of one molecule relative to its neighbors along the stacking direction has been shown to be due to the symmetry (or nodal) properties of the LUMO of the TCNQ molecule (Berlinsky, Carolan & Weiler, 1976). The similarity in the acceptor overlaps for the two compounds can be readily understood, since the nodal properties of the LUMO of the tetrahalo-*p*-benzoquinones is the same as that of TCNQ, which is why we chose that class of molecules as likely candidates to form segregated stacks in the first place (Torrance *et al.*, 1979).

A crucial difference between the acceptor stacks in the two structures is the magnitude of the interplanar spacing. In TMTTF–TCNQ the TCNQ molecules are 3·27 Å apart. In the bromanil analog, the acceptor molecules are separated by 3·37 Å. This 0·1 Å difference in the interplanar separation of the acceptor molecules is the most noteworthy structural difference between the two materials. The poorer electronic overlap that this causes may well be responsible for the fact that the 300 K conductivity of TMTTF–brl is activated (Torrance *et al.*, 1979, 1981) whereas that of TMTTF–TCNQ is metallic (Carruthers, Bloch & Cowan, 1976). The large interplanar spacing of the bromanil molecules is most likely caused by the bulk of the Br atoms. The closest intermolecular Br—Br distance within a stack is 3·853 Å, compared to a value of 3·90 Å for twice the van der Waals radius of Br (Pauling, 1960). Any decrease in the interplanar spacing, without an accompanying sideways slippage of the molecules, appears to be prohibited by what would be an increasingly repulsive Br—Br interaction.

There are also similarities between these two structures with respect to the relation of one stack to another. As shown in Figs. 1(*a*) and 2(*a*), both structures are such that donors and acceptors are arranged in a head-to-tail fashion in a direction parallel to their long molecular dimensions. In the primitive ($P2/c$) structure of the TCNQ salt this is the [101] direction. In the centered ($C2/c$) structure of the bromanil salt the analogous direction is [102]. Projections of the TCNQ and bromanil salts onto the ($10\bar{1}$) and ($20\bar{1}$) planes, respectively, are shown in Figs. 2(*b*) and 1(*b*). The difference in the two structures is that in the ($10\bar{1}$) plane of the TCNQ salt both donor and acceptor stacks are tilted in the same direction with respect to the stacking axis whereas in the $(20\bar{1})$ plane of the bromanil salt the donor and acceptor stacks are tilted in opposite directions to each other. In addition, there is a slight difference in the relative arrangements of the stacks in the direction normal to the $(20\bar{1})$ plane of the bromanil salt compared to the arrangement perpendicular to the $(10\bar{1})$ plane of the TCNQ salt. This difference can also be seen by comparison of Figs. 1(*b*) and 2(*b*).

Conclusion

In this paper we have reported the structure of the first 1:1 organic charge-transfer salt to exhibit segregated stacking of donors and acceptors that does not contain TCNQ or a TCNQ-like molecule. The striking similarity that the structure of TMTTF–brl bears to that of TMTTF–TCNQ (Phillips *et al.*, 1976) has been demonstrated. The most noteworthy difference between the two structures is the difference in the interplanar spacing of the acceptor molecules. The 0·1 Å larger spacing in TMTTF–brl is probably caused by the bulk of the Br atoms. A similar effect occurs in the dibenzotetrathiafulvalene (DBTTF) salt of $TCNQCl_2$, in which the 3·41 Å spacing (Soling, Rindorf & Thorup, 1981) between acceptor molecules is presumably caused by the bulk of the Cl atoms. The resultant weakening of the intermolecular π overlap in the acceptor stacks of these materials is probably related to the appreciably lower conductivity of TMTTF–brl and DBTTF–$TCNQCl_2$ (Jacobsen, Pedersen, Mortensen & Bechgaard, 1980) compared to that of TMTTF–TCNQ.

References

Berlinsky, A. J., Carolan, J. F. & Weiler, L. (1976). *Solid State Commun.* **19**, 1165–1168.

Carruthers, T., Bloch, A. N. & Cowan, D. O. (1976). *Bull. Am. Phys. Soc.* **21**, 213.

Crowley, J. I. (1980). Private communication.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Jacobsen, C. S., Pedersen, H. J., Mortensen, K. & Bechgaard, K. (1980). *J. Phys. C*, **13**, 3411–3425.

Mayerle, J. J. (1977). *Inorg. Chem.* **16**, 916–919.

Mayerle, J. J. (1980). *Mixed-Valence Compounds*, edited by D. B. Brown, pp. 451–473. Dordrecht: Reidel.

Mayerle, J. J. & Torrance, J. B. (1980*a*). *Bull. Chem. Soc. Jpn.* Submitted.

Mayerle, J. J. & Torrance, J. B. (1980*b*). Unpublished results.

Mayerle, J. J., Torrance, J. B. & Crowley, J. I. (1979). *Acta Cryst.* B**35**, 2988–2995.

Metzger, R. M. (1978). Private communication.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.

Phillips, T. E., Kistenmacher, T. J., Bloch, A. N., Ferraris, J. P. & Cowan, D. O. (1976). *Acta Cryst.* B**33**, 422–428.

Soling, H., Rindorf, G. & Thorup, N. (1981). *Acta Cryst.* B**37**, 1716–1719.

Torrance, J. B. (1979). *Acc. Chem. Res.* **12**, 79–86.

Torrance, J. B., Mayerle, J. J., Lee, V. Y. & Bechgaard, K. (1979). *J. Am. Chem. Soc.* **101**, 4747–4748.

Torrance, J. B., Mayerle, J. J., Lee, V. Y., Bozio, R. & Pecile, C. (1981). *Solid State Commun.* Submitted.

Acta Cryst. (1981). B**37**, 2034–2043

The Structures of *N*-(*n*-Propyl)pyridinium–7,7,8,8-Tetracyano-*p*-quinodimethane (1:2) [$NPPy^+.(TCNQ)_2^-$] and *N*-(*n*-Butyl)pyridinium–7,7,8,8-Tetracyano-*p*-quinodimethane (4:7) [$(NBPy^+)_4.(TCNQ)_7^{4-}$]

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(*Received* 13 *November* 1980; *accepted* 6 *April* 1981)

Abstract

The crystal structures of $NPPy^+.(TCNQ)_2^-$ and $(NBPy^+)_4.(TCNQ)_7^{4-}$ have been determined at 297 K by X-ray diffraction. Crystals of the former are triclinic with space group $P\bar{1}$, a = 14·5419 (19), b = 13·7233 (14), c = 7·8016 (9) Å, α = 104·059 (10), β = 110·723 (12), γ = 94·084 (11)°, V = 1391·2 (2) Å^3 and Z = 2. Those of the latter are triclinic with space group $P\bar{1}$, a = 15·0448 (10), b = 17·3667 (14), c = 10·4666 (9) Å, α = 105·557 (7), β = 98·007 (7), γ = 96·913 (6)°, V = 2572·9 (3) Å^3 and Z = 1. Refine-

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0567-7408/81/112034-10\$01.00