Perkins, M. J., Setchell, P. K. & Williams, D. J. (1993). *J. Chem. Soc. Chem. Commun.* pp. 128-129.

Sharma, H. K., Cervantes-Lee, F. & Pannell, K. H. (1992). *J. Organomet. Chem.* **438**, 183-194.

Shubina, E. S., Epstein, L. M., Kreindlin, A. Z., Fadeeva, S. S. & Rybinskaya, M. I. (1991). *J. Organomet. Chem.* **401**, 145-153.

Shubina, E. S., Epstein, L. M., Slovokhotov, Yu. L., Mironov, A. V., Struchkov, Yu. T., Kaganovich, V. S., Kreindlin, A. Z. & Rybinskaya, M. I. (1991). *J. Organomet. Chem.* **401**, 155-165.

Shubina, E. S., Epstein, L. M., Timofeeva, T. V., Struchkov, Yu. T., Kreindlin, A. Z., Fadeeva, S. S. & Rybinskaya, M. I. (1991). *J. Organomet. Chem.* **401**, 133-143.

Shubina, E. S., Epstein, L. M., Yanovsky, Y. I., Timofeeva, T. V., Struchkov, Yu. T., Kreindlin, A. Z., Fadeeva, S. S. & Rybinskaya, M. I. (1988). *J. Organomet. Chem.* **345**, 313-320.

Spek, A. L. (1991). *PLATON. Molecular Geometry Program*. Univ. of Utrecht, The Netherlands.

Spek, A. L. (1991). *PLUTON. Molecular Graphics Program*. Univ. of Utrecht, The Netherlands.

Struchkov, Yu. T., Batsanov, A. S., Toma, S. & Salisova, M. (1987). *J. Organomet. Chem.* **329**, 375-379.

Yamakawa, K. & Hisatome, M. (1973). *J. Organomet. Chem.* **52**, 407-424.

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*Acta Cryst.* (1994). **C50**, 23–25

# Structure of (BEDT-TTF)$_4$[Hg$_2$Br$_6$].THF

JAMES THIEL, XIANHUI BU AND PHILIP COPPENS

*Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, USA*

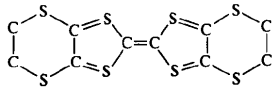
(*Received* 4 *June* 1992; *accepted* 2 *July* 1993)

## Abstract

The structure of tetrakis[3,4;3′4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalen]ium hexabromodimercurate tetrahydrofuran consists of two-dimensional sheets of BEDT-TTF separated by $Hg_2Br_6^{2-}$ anions and THF molecules centered at $x = 0$.

## Comment

As a result of their unusual transport properties, salts of BEDT-TTF have attracted considerable attention (Williams *et al.*, 1987). Of particular interest are the organomineral salts, which show the highest superconducting transition temperatures in the BEDT-TTF family or in other organic salts. We report here the crystal structure of a newly synthesized salt, (BEDT-TTF)$_4$[Hg$_2$Br$_6$].THF.



The anion is different from that found in (BEDT-TTF)$_4$[HgBr$_4$].TCE (TCE = 1,1,2-trichloroethane) (Bu, Coppens & Naughton, 1990), but comparable to the $Hg_2I_6$ anion in (BEDT-TTF)$_4$[Hg$_2$I$_6$][I$_8$] (Bu & Coppens, 1992).

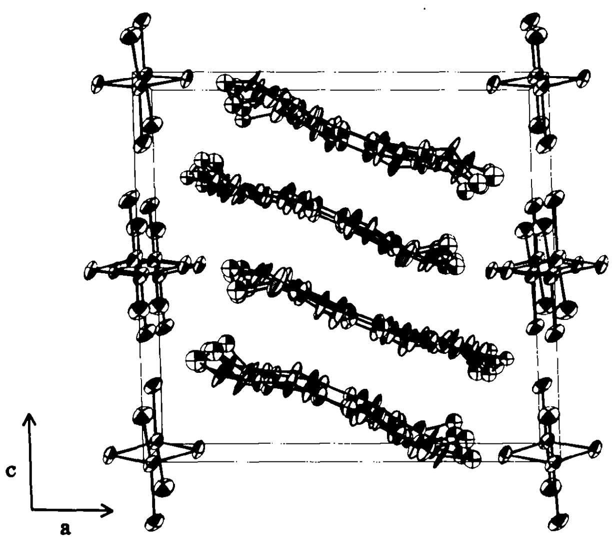


Fig. 1. The unit-cell packing diagram viewed along the *b* axis. Thermal ellipsoids are drawn at the 50% probability level. The THF molecule is omitted.

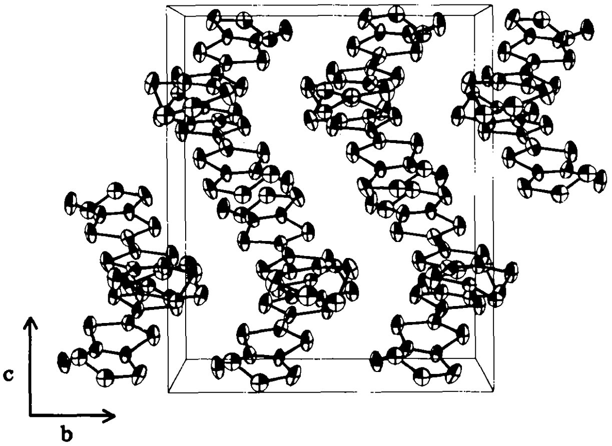


Fig. 2. The unit-cell packing diagram viewed along the *a* axis. Thermal ellipsoids are drawn at the 50% probability level. Only the BEDT-TTF molecules are shown.

## Experimental

*Crystal data*

$4C_{10}H_8S_8[Hg_2Br_6]$.-
$C_4H_8O$
$M_r = 2491.3$
Monoclinic
$P2_1/c$
$a = 17.080$ (2) Å
$b = 13.467$ (3) Å
$c = 15.991$ (4) Å

$D_x = 2.25$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17-19°$
$\mu = 8.31$ mm$^{-1}$
$T = 293$ K

*Acta Crystallographica Section C*
ISSN 0108-2701 ©1994

$\beta = 91.68\ (1)^\circ$
$V = 3677\ (2)\ \text{Å}^3$
$Z = 2$

Plate
$0.38 \times 0.32 \times 0.04$ mm
Black

*Data collection*

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.13$, $T_{\max} = 0.69$
6699 measured reflections
6699 independent reflections

3724 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 25^\circ$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 300 min
intensity variation: −4.8%

*Refinement*

Refinement on $F$
$R = 0.049$
$wR = 0.053$
$S = 2.87$
3575 reflections
331 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$\Delta\rho_{\max} = 1.9\ \text{e Å}^{-3}$
$\Delta\rho_{\min} = -1.2\ \text{e Å}^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Data collection: Enraf-Nonius CAD-4 software. Data reduction: *Structure Determination Package* (Enraf-Nonius, 1985). Program(s) used to solve structure: *Structure Determination Package*. Program(s) used to refine structure: *Structure Determination Package*. Molecular graphics: Nicolet X-ray products. Software used to prepare material for publication: *Structure Determination Package*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Hg | −0.00013 (3) | 0.14487 (5) | 0.47726 (3) | 0.0509 (1) |
| Br1 | −0.11334 (8) | −0.0026 (1) | 0.49248 (8) | 0.0460 (4) |
| Br2 | −0.0118 (1) | 0.2443 (1) | 0.60788 (9) | 0.0679 (5) |
| Br3 | 0.0056 (1) | 0.1914 (1) | 0.32679 (8) | 0.0666 (5) |
| S1*a* | 0.6387 (2) | 0.2173 (3) | 0.7916 (2) | 0.0453 (9) |
| S1*b* | 0.6503 (2) | 0.7164 (3) | 0.8163 (2) | 0.049 (1) |
| S2*a* | 0.5981 (2) | 0.0087 (2) | 0.8191 (2) | 0.047 (1) |
| S2*b* | 0.6056 (2) | 0.5092 (3) | 0.8315 (2) | 0.049 (1) |
| S3*a* | 0.4699 (2) | 0.2830 (3) | 0.8642 (2) | 0.050 (1) |
| S3*b* | 0.4857 (2) | 0.7840 (3) | 0.8893 (2) | 0.050 (1) |
| S4*a* | 0.4314 (2) | 0.0734 (3) | 0.8883 (2) | 0.049 (1) |
| S4*b* | 0.4389 (2) | 0.5773 (3) | 0.9041 (2) | 0.050 (1) |
| S5*a* | 0.8080 (2) | 0.1800 (3) | 0.7730 (2) | 0.059 (1) |
| S5*b* | 0.8149 (2) | 0.6796 (3) | 0.7809 (2) | 0.056 (1) |
| S6*a* | 0.7617 (2) | −0.0636 (3) | 0.8013 (2) | 0.058 (1) |
| S6*b* | 0.7605 (2) | 0.4291 (3) | 0.7903 (2) | 0.055 (1) |
| S7*a* | 0.3283 (2) | 0.3557 (3) | 0.9509 (2) | 0.060 (1) |
| S7*b* | 0.3433 (2) | 0.8637 (3) | 0.9671 (2) | 0.062 (1) |
| S8*a* | 0.2875 (2) | 0.1099 (3) | 0.9808 (2) | 0.057 (1) |
| S8*b* | 0.2897 (2) | 0.6171 (3) | 0.9837 (2) | 0.053 (1) |
| C1*a* | 0.5703 (7) | 0.1343 (9) | 0.8277 (7) | 0.039 (3) |
| C1*b* | 0.5811 (7) | 0.6321 (9) | 0.8440 (7) | 0.041 (3) |
| C2*a* | 0.5002 (7) | 0.1613 (9) | 0.8582 (7) | 0.040 (3) |
| C2*b* | 0.5090 (7) | 0.6612 (9) | 0.8759 (7) | 0.041 (4) |
| C3*a* | 0.7159 (7) | 0.1312 (9) | 0.7923 (6) | 0.037 (3) |
| C3*b* | 0.7242 (7) | 0.628 (1) | 0.8012 (7) | 0.040 (4) |
| C4*a* | 0.6968 (7) | 0.0359 (9) | 0.8050 (7) | 0.040 (3) |
| C4*b* | 0.7025 (7) | 0.5316 (9) | 0.8078 (7) | 0.036 (3) |
| C5*a* | 0.3862 (7) | 0.2567 (9) | 0.9213 (7) | 0.040 (4) |
| C5*b* | 0.3964 (7) | 0.7603 (9) | 0.9373 (7) | 0.038 (3) |
| C6*a* | 0.3688 (7) | 0.1602 (8) | 0.9329 (7) | 0.035 (3) |
| C6*b* | 0.3754 (7) | 0.6651 (8) | 0.9440 (7) | 0.034 (3) |
| C7*a* | 0.865 (1) | 0.074 (1) | 0.7373 (9) | 0.076 (5) |
| C7*b* | 0.8755 (8) | 0.570 (1) | 0.7653 (7) | 0.053 (4) |
| C8*a* | 0.823 (1) | −0.018 (1) | 0.7168 (9) | 0.073 (5) |
| C8*b* | 0.8361 (9) | 0.483 (1) | 0.7241 (8) | 0.058 (4) |
| C9*a* | 0.2335 (9) | 0.298 (1) | 0.9279 (8) | 0.068 (4) |
| C9*b* | 0.245 (1) | 0.815 (1) | 0.9428 (8) | 0.071 (5) |
| C10*a* | 0.217 (1) | 0.212 (1) | 0.9822 (8) | 0.069 (4) |
| C10*b* | 0.2286 (9) | 0.724 (1) | 0.9973 (8) | 0.068 (4) |
| O | 0.001 (1) | 0.030 (2) | −0.072 (1) | 0.086 (7) |
| C21 | −0.065 (1) | 0.014 (1) | −0.025 (1) | 0.1 |
| C22 | 0.071 (1) | 0.022 (1) | −0.041 (1) | 0.1 |

Table 2. *Geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Hg—Br1 | 2.7870 (9) | S5*b*—C7*b* | 1.825 (9) |
| Hg—Br1 | 2.7583 (9) | S6*a*—C4*a* | 1.741 (8) |
| Hg—Br2 | 2.4940 (9) | S6*a*—C8*a* | 1.842 (9) |
| Hg—Br3 | 2.4911 (8) | S6*b*—C4*b* | 1.728 (8) |
| S1*b*—C1*b* | 1.708 (8) | S6*b*—C8*b* | 1.841 (8) |
| S1*b*—C3*b* | 1.758 (8) | S7*a*—C5*a* | 1.734 (8) |
| S1*a*—C1*a* | 1.729 (7) | S7*a*—C9*a* | 1.82 (1) |
| S1*a*—C3*a* | 1.755 (8) | S7*b*—C5*b* | 1.735 (8) |
| S2*b*—C1*b* | 1.720 (8) | S7*b*—C9*b* | 1.83 (1) |
| S2*b*—C4*b* | 1.735 (7) | S8*b*—C6*b* | 1.736 (7) |
| S2*a*—C1*a* | 1.764 (8) | S8*b*—C10*b* | 1.80 (1) |
| S2*a*—C4*a* | 1.746 (8) | S8*a*—C6*a* | 1.742 (7) |
| S3*a*—C2*a* | 1.722 (7) | S8*a*—C10*a* | 1.83 (1) |
| S3*a*—C5*a* | 1.755 (8) | C1*a*—C2*a* | 1.36 (1) |
| S3*b*—C2*b* | 1.716 (8) | C1*b*—C2*b* | 1.40 (1) |
| S3*b*—C5*b* | 1.756 (7) | C3*b*—C4*b* | 1.35 (1) |
| S4*b*—C2*b* | 1.716 (8) | C3*a*—C4*a* | 1.34 (1) |
| S4*b*—C6*b* | 1.740 (7) | C5*b*—C6*b* | 1.337 (9) |
| S4*a*—C2*a* | 1.746 (8) | C5*a*—C6*a* | 1.35 (1) |
| S4*a*—C6*a* | 1.751 (7) | C7*b*—C8*b* | 1.49 (1) |
| S5*a*—C3*a* | 1.740 (7) | C7*a*—C8*a* | 1.46 (1) |
| S5*a*—C7*a* | 1.83 (1) | C9*b*—C10*b* | 1.52 (1) |
| S5*b*—C3*b* | 1.739 (8) | C9*a*—C10*a* | 1.48 (1) |
| Br1—Hg—Br1$^{\rm i}$ | 88.59 (3) | S4*a*—C2*a*—C1*a* | 121.7 (6) |
| Br1—Hg—Br2 | 103.67 (3) | S1*b*—C3*b*—S5*b* | 113.6 (5) |
| Br1—Hg—Br3 | 108.09 (3) | S1*b*—C3*b*—C4*b* | 116.1 (6) |
| Br1$^{\rm i}$—Hg—Br2 | 107.41 (3) | S5*b*—C3*b*—C4*b* | 130.3 (6) |
| Br1$^{\rm i}$—Hg—Br3 | 107.26 (3) | S1*a*—C3*a*—S5*a* | 115.5 (5) |
| Br2—Hg—Br3 | 132.88 (4) | S1*a*—C3*a*—C4*a* | 116.5 (6) |
| Hg—Br1—Hg$^{\rm i}$ | 91.41 (3) | S5*a*—C3*a*—C4*a* | 127.9 (6) |
| C1*b*—S1*b*—C3*b* | 95.1 (4) | S2*b*—C4*b*—S6*b* | 116.9 (4) |
| C1*a*—S1*a*—C3*a* | 94.9 (4) | S2*b*—C4*b*—C3*b* | 116.7 (6) |
| C1*b*—S2*b*—C4*b* | 95.4 (4) | S6*b*—C4*b*—C3*b* | 126.3 (6) |
| C1*a*—S2*a*—C4*a* | 94.1 (4) | S2*a*—C4*a*—S6*a* | 117.5 (5) |
| C2*a*—S3*a*—C5*a* | 95.1 (4) | S2*a*—C4*a*—C3*a* | 117.4 (6) |
| C2*b*—S3*b*—C5*b* | 95.0 (4) | S6*a*—C4*a*—C3*a* | 124.9 (6) |
| C2*b*—S4*b*—C6*b* | 95.5 (4) | S3*b*—C5*b*—S7*b* | 116.2 (4) |
| C2*a*—S4*a*—C6*a* | 94.8 (3) | S3*b*—C5*b*—C6*b* | 116.6 (6) |
| C3*a*—S5*a*—C7*a* | 104.7 (4) | S7*b*—C5*b*—C6*b* | 127.1 (6) |
| C3*b*—S5*b*—C7*b* | 102.3 (4) | S3*a*—C5*a*—S7*a* | 117.9 (4) |
| C4*a*—S6*a*—C8*a* | 98.4 (4) | S3*a*—C5*a*—C6*a* | 116.9 (6) |
| C4*b*—S6*b*—C8*b* | 101.1 (4) | S7*a*—C5*a*—C6*a* | 125.1 (6) |
| C5*a*—S7*a*—C9*a* | 97.3 (4) | S4*b*—C6*b*—S8*b* | 115.0 (4) |
| C5*b*—S7*b*—C9*b* | 97.8 (4) | S4*b*—C6*b*—C5*b* | 116.8 (6) |
| C6*b*—S8*b*—C10*b* | 104.1 (4) | S8*b*—C6*b*—C5*b* | 128.1 (6) |
| C6*a*—S8*a*—C10*a* | 104.3 (4) | S4*a*—C6*a*—S8*a* | 115.1 (4) |
| S1*a*—C1*a*—S2*a* | 114.1 (4) | S4*a*—C6*a*—C5*a* | 116.7 (6) |
| S1*a*—C1*a*—C2*a* | 124.0 (6) | S8*a*—C6*a*—C5*a* | 128.1 (6) |
| S2*a*—C1*a*—C2*a* | 121.9 (6) | S5*b*—C7*b*—C8*b* | 116.4 (6) |
| S1*b*—C1*b*—S2*b* | 115.9 (4) | S5*a*—C7*a*—C8*a* | 118.0 (7) |
| S1*b*—C1*b*—C2*b* | 122.0 (6) | S6*b*—C8*b*—C7*b* | 111.7 (5) |
| S2*b*—C1*b*—C2*b* | 122.1 (6) | S6*a*—C8*a*—C7*a* | 113.9 (6) |
| S3*b*—C2*b*—S4*b* | 115.8 (4) | S7*b*—C9*b*—C10*b* | 110.4 (7) |
| S3*b*—C2*b*—C1*b* | 121.7 (6) | S7*a*—C9*a*—C10*a* | 113.5 (7) |
| S4*b*—C2*b*—C1*b* | 122.5 (6) | S8*b*—C10*b*—C9*b* | 116.9 (7) |
| S3*a*—C2*a*—S4*a* | 115.1 (4) | S8*a*—C10*a*—C9*a* | 116.4 (7) |
| S3*a*—C2*a*—C1*a* | 123.1 (6) | | |

Symmetry code: (i) $-x, -y, 1-z$.

The crystal was synthesized by electrocrystallization of a THF solution containing 1.51 m$M$ BEDT-TTF and 22.7 m$M$ ($n$-butyl)$_4$NHgBr$_3$ at 0.4 μA. The structure was solved by heavy-atom methods and subsequent Fourier methods using the Enraf-Nonius *Structure Determination Package* (Enraf-Nonius, 1985). No H atoms were included in the refinement. The weighting scheme was $w = 1/\sigma^2(F)$; $\sigma(F) = \sigma(F^2)/2F$; $\sigma(F^2) = [\sigma_{cs}^2 + (0.02|F|^2)^2]^{1/2}$. A solvent molecule (THF) is incorporated in the structure. It is disordered about the inversion site at the origin. As the C atoms of the inversion-center-related disodered THF molecules are approximately superimposed, only two THF C atoms were included with full occupancy.

Support of this work by the Petroleum Research Fund administered by the American Chemical Society (PRF21392-AC6-C) and the National Science Foundation (CHE9021069) is gratefully acknowledged.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71457 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1027]

## References

Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.

Bu, X. & Coppens, P. (1992). *Acta Cryst.* C**48**, 1565-1566.

Bu, X., Coppens, P. & Naughton, M. (1990). *Acta Cryst.* C**46**, 1609-1612.

Williams, J. M., Wang, H. H., Emge, T. J., Geiser, U., Beno, M. A., Leung, P. C. W., Carlson, K. D., Thorn, R. J., Schultz, A. J. & Whangbo, M. H. (1987). *Progress in Inorganic Chemistry*, Vol. 35, edited by S. Lippard, pp. 51-218. New York: John Wiley.

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*Acta Cryst.* (1994). C**50**, 25–27

# 4-Methoxy-1-[(1$R$,4$S$,5$R$)-8-phenylmenthoxycarbonyl]pyridinium Hexachloroantimonate, $C_{23}H_{30}NO_3^+.SbCl_6^-$

PHIRTU SINGH, DANIEL L. COMINS AND SAJAN P. JOSEPH

*Department of Chemistry,*
*North Carolina State University, Raleigh,*
*NC 27695-8204, USA*

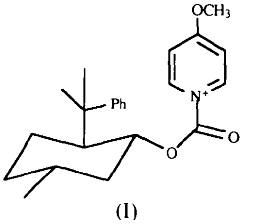
(*Received* 5 *January* 1993; *accepted* 14 *June* 1993)

## Abstract

The 4-methoxypyridinium and oxycarbonyl moieties are coplanar and approximately parallel to the phenyl ring. The latter is involved in a number of short intramolecular interactions with the pyridinium and the oxycarbonyl atoms. Crystal packing is characterized by the presence of hydrophobic and hydrophilic channels, the former consisting of phenylmenthyl groups and the latter of pyridinium and $SbCl_6^-$ ions.

## Comment

The structure determination of the title compound was undertaken to establish the conformation of the cation (I). This is the first non-racemic $N$-acylpyridinium salt prepared in crystalline form. Chiral salts of this type have been prepared *in situ* and reacted with Grignard reagents to give synthetically useful 1-acyl-2-alkyl-2,3-dihydro-4(1$H$)-pyridinones (Comins, Goehring, Joseph & O'Connor, 1990; Comins & Hong, 1991; Comins & Dehghani, 1991; Comins, Hong & Salvador, 1991; Comins & LaMunyon, 1992; Comins & Killpack, 1993).



(I)

The X-ray work described here shows that the 4-methoxypyridinium moiety and the oxycarbonyl group, O(3)—C(7)—O(2) (Fig. 1), are coplanar, the deviations from the mean plane being C(1) −0.016, O(1) −0.010, C(2) −0.014, C(3) 0.026, C(4) 0.016, N(1) −0.013, C(5) 0.016, C(6) 0.019, C(7) −0.005, O(2) −0.014 and O(3) −0.006 Å. Atom C(8) of the cyclohexane ring lies close to this plane, deviating by only −0.073 Å. A similar coplanar arrangement of the oxycarbonyl group and the pyridinium moiety was observed in $N$-phenoxycarbonyl-4-dimethylaminopyridinium chloride (Bryant & King, 1992), which suggests possible conjugation between the oxycarbonyl and pyridine moieties in these compounds. The dihedral angle between the oxycarbonylpyridinium plane and the phenyl ring is 13.7°. They are, therefore, approximately parallel and in a favorable orientation for π–π stacking interactions. The phenyl ring interacts primarily with atoms C(4), N(1), C(7) and O(3) of the oxycarbonylpyridinium moiety (Fig. 1 and Table 3). The intramolecular interactions observed here are similar to, but more numerous than, those observed in a related neutral molecule reported previously from this laboratory (Singh, Comins & Killpack, 1990). The oxycarbonylpyridinium and the phenyl moieties, being bulky, occupy equatorial sites on the cyclohexane ring.

*Acta Crystallographica Section C*
ISSN 0108-2701 © 1994