

References

- BEURSKENS, P. T. (1984). Tech. Report 1984. Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, The Netherlands.
- GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- KAPLAN, H. R., WOLKE, R. E. & MALONE, M. H. (1967). *J. Pharm. Sci.* **56**, 1385–1392.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- PARODI, S., FLORA, S. D., CAVANNA, M., PINO, A., ROBBIANO, L., BENNICELLI, C. & BRAMBILLA, G. (1981). *Cancer Res.* **41**, 1469–1482.
- RODI, Y. K., LOPEZ, L., MALAUAUD, C., BOISDON, M. T. & BARRANS, J. (1991). *J. Chem. Soc. Chem. Commun.* pp. 23–24.

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Structure of the Cation Radical Salt 3,8-Dimethoxy-1,6-dithiapyrenium Hexafluorophosphate

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Abstract. $C_{16}H_{12}O_2S_2^+ \cdot PF_6^-$, $M_r = 445.35$, orthorhombic, $Cmca$, $a = 6.628$ (4), $b = 21.495$ (6), $c = 23.526$ (6) Å, $V = 3352$ (2) Å³, $Z = 8$, $D_x = 1.765$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 4.70$ cm⁻¹, $F(000) = 1800$, $T = 294$ K, $R = 0.065$ for 629 observed reflections. The structure consists of segregated stacks along the a axis of flat organic cations spaced by $\frac{1}{2}a = 3.314$ Å. A short S...S distance of 3.348 (2) Å is found within the organic stack. The surrounding anions have disordered F atoms.

Experimental. Small needle-shaped crystals of the title compound were grown by electrochemical oxidation of 3,8-dimethoxy-1,6-dithiapyrene in CH₂Cl₂ containing (*n*-Bu)₄NPF₆. A single crystal with dimensions 0.30 × 0.09 × 0.03 mm was selected for study on an Enraf–Nonius CAD-4 diffractometer with graphite monochromator. The unit cell was derived from settings of 22 reflections having 4.5 < θ < 9.5°. Intensity data were collected in ω -scan mode with $\Delta\omega = (0.80 + 0.35\tan\theta)^\circ$ within the range 0 < θ < 20°, $-6 \leq h \leq 6$, $-20 \leq k \leq 20$, $0 \leq l \leq 22$ (the low cut-off angle was used because of weak scattering at higher θ). No significant decay was observed for the three intensity control reflections. Corrections for Lorentz, polarization and absorption (Gaussian integration, transmission 0.96–0.99) effects were applied. A total of 3177 reflections were measured, and after

removal of systematic absences these were merged to 880 unique reflections, $R_{int}(F) = 0.026$. The systematic absences were consistent with space groups $Cmca$ and $Aba2$. The structure was solved in the former space group by direct methods using *SHELXS86* (Sheldrick, 1990). 629 reflections having $I > 2\sigma(I)$ were included in the least-squares refinement of the structure (on F) using *SHELX76* (Sheldrick, 1976). Complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All atoms of the organic cation except two methyl H atoms were located and kept fixed on the mirror plane perpendicular to the a axis. The P atom of the PF₆⁻ cation was also restricted to the mirror plane. Four F atoms were fairly close to this plane, but their displacement parameters became physically unreasonable if the atoms were constrained to the mirror plane. Therefore, a disordered model for PF₆⁻ with split F-atom positions was introduced. One set of F-atom positions is related to the other set by the mirror plane operation, and the two sets of positions are equally occupied. Removal of the mirror plane and refinement in the non-centrosymmetric space group $Aba2$ was also attempted, but the deviations of the resultant positions from the 'in-plane' positions were small and the associated e.s.d.'s quite large. In addition, the latter refinement involved severe correlations and the resultant thermal parameters of F atoms were still unreasonable. Therefore,

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) of the non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

| | x | y | z | U_{eq} |
|-------|-----------|----------|----------|----------|
| S(1) | 0 | 4891 (2) | 2602 (2) | 56 (2) |
| S(2) | 0 | 1770 (2) | 2097 (2) | 54 (2) |
| O(1) | 0 | 2718 (5) | 647 (4) | 66 (3) |
| O(2) | 0 | 3941 (4) | 4047 (4) | 61 (3) |
| C(1) | 0 | 4192 (5) | 2249 (5) | 42 (3) |
| C(2) | 0 | 4223 (6) | 1649 (6) | 44 (4) |
| C(3) | 0 | 3706 (6) | 1314 (6) | 46 (4) |
| C(4) | 0 | 3113 (5) | 1570 (5) | 42 (3) |
| C(5) | 0 | 3060 (5) | 2181 (5) | 39 (3) |
| C(6) | 0 | 3601 (5) | 2530 (5) | 41 (3) |
| C(7) | 0 | 3555 (6) | 3132 (5) | 45 (3) |
| C(8) | 0 | 4093 (6) | 3485 (6) | 52 (4) |
| C(9) | 0 | 4688 (6) | 3300 (6) | 50 (4) |
| C(10) | 0 | 2570 (6) | 1211 (6) | 48 (4) |
| C(11) | 0 | 1984 (6) | 1400 (6) | 52 (4) |
| C(12) | 0 | 2473 (5) | 2458 (5) | 40 (3) |
| C(13) | 0 | 2437 (7) | 3041 (6) | 53 (4) |
| C(14) | 0 | 2962 (6) | 3375 (7) | 50 (4) |
| C(15) | 0 | 2221 (9) | 224 (9) | 81 (6) |
| C(16) | 0 | 4433 (8) | 4461 (8) | 73 (6) |
| P | 5000 | 919 (2) | 764 (2) | 53 (2) |
| F(1) | 4526 (17) | 1640 (4) | 862 (3) | 58 (3) |
| F(2) | 5368 (25) | 191 (4) | 669 (3) | 66 (4) |
| F(3) | 5824 (15) | 824 (5) | 1391 (5) | 84 (4) |
| F(4) | 4221 (16) | 1016 (5) | 146 (5) | 79 (4) |
| F(5) | 7279 (25) | 956 (7) | 557 (8) | 116 (5) |
| F(6) | 2802 (25) | 857 (7) | 998 (8) | 113 (5) |

least-squares refinement in space group $Cmca$ with disordered F atoms was preferred with the present data. A more extensive set of data (e.g. at low temperature) might lead to a different choice. The final model, with 120 parameters, had anisotropic displacement parameters for S and P atoms and isotropic for C, O and F atoms. For all H atoms a fixed value of $U_{iso} = 0.06 \text{\AA}^2$ was used. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma_{count}^2(F_o) + 0.0004|F_c|^2]^{-1}$. The final agreement factors were $R(F) = 0.065$, $wR(F) = 0.078$ and $S = 2.94$. The somewhat high residuals are probably a result of the rather crude structure model with isotropic displacements for most atoms. Maximum (Δ/σ) in the final cycle was 0.002 and maximum and minimum residual electron density was 0.65 and -0.46 e \AA^{-3} . Positional and thermal parameters are given in Table 1.* For molecular geometry calculations *PLATON* (Spek, 1990) was used and crystal-structure illustrations were produced by *PLUTO* (Motherwell & Clegg, 1978) and *ORTEPII* (Johnson, 1976).

The atomic numbering of the constituents is shown in Fig. 1. Bond lengths and bond angles are given in Table 2. By symmetry, the organic cation is strictly planar (except for four H atoms). A similar

* Lists of anisotropic displacement parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55261 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0275]

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

| | | | |
|------------------|------------|-------------------|------------|
| S(1)—C(1) | 1.716 (12) | C(5)—C(12) | 1.420 (16) |
| S(1)—C(9) | 1.699 (15) | C(6)—C(7) | 1.420 (17) |
| S(2)—C(11) | 1.702 (15) | C(7)—C(8) | 1.424 (18) |
| S(2)—C(12) | 1.734 (12) | C(7)—C(14) | 1.397 (19) |
| O(1)—C(10) | 1.364 (17) | C(8)—C(9) | 1.351 (18) |
| O(1)—C(15) | 1.460 (20) | C(10)—C(11) | 1.336 (18) |
| O(2)—C(8) | 1.362 (17) | C(12)—C(13) | 1.374 (18) |
| O(2)—C(16) | 1.440 (20) | C(13)—C(14) | 1.380 (20) |
| C(1)—C(2) | 1.413 (18) | P—F(1) | 1.599 (9) |
| C(1)—C(6) | 1.432 (16) | P—F(2) | 1.599 (9) |
| C(2)—C(3) | 1.362 (19) | P—F(3) | 1.587 (12) |
| C(3)—C(4) | 1.410 (17) | P—F(4) | 1.556 (12) |
| C(4)—C(5) | 1.442 (17) | P—F(5) | 1.589 (20) |
| C(4)—C(10) | 1.441 (17) | P—F(6) | 1.565 (20) |
| C(5)—C(6) | 1.424 (16) | | |
| C(1)—S(1)—C(9) | 104.1 (6) | O(1)—C(10)—C(4) | 112.4 (11) |
| C(11)—S(2)—C(12) | 103.7 (6) | O(1)—C(10)—C(11) | 122.9 (13) |
| C(10)—O(1)—C(15) | 119.5 (12) | C(4)—C(10)—C(11) | 124.7 (13) |
| C(8)—O(2)—C(16) | 118.8 (11) | S(2)—C(11)—C(10) | 125.1 (11) |
| S(1)—C(2)—C(2) | 116.2 (9) | S(2)—C(12)—C(5) | 123.3 (9) |
| S(1)—C(1)—C(6) | 123.6 (9) | S(2)—C(12)—C(13) | 116.1 (9) |
| C(2)—C(1)—C(6) | 120.2 (10) | C(5)—C(12)—C(13) | 120.5 (11) |
| C(1)—C(2)—C(3) | 122.6 (12) | C(12)—C(13)—C(14) | 121.6 (13) |
| C(2)—C(3)—C(4) | 119.4 (13) | C(7)—C(14)—C(13) | 121.0 (14) |
| C(3)—C(4)—C(5) | 119.8 (10) | F(1)—P—F(2) | 177.5 (6) |
| C(3)—C(4)—C(10) | 118.8 (11) | F(1)—P—F(3) | 93.3 (5) |
| C(5)—C(4)—C(10) | 121.4 (10) | F(1)—P—F(4) | 86.5 (5) |
| C(4)—C(5)—C(6) | 120.7 (10) | F(1)—P—F(5) | 100.5 (7) |
| C(4)—C(5)—C(12) | 121.8 (10) | F(1)—P—F(6) | 81.3 (7) |
| C(6)—C(5)—C(12) | 117.5 (10) | F(2)—P—F(3) | 87.2 (5) |
| C(1)—C(6)—C(5) | 117.3 (10) | F(2)—P—F(4) | 93.0 (5) |
| C(1)—C(6)—C(7) | 121.5 (10) | F(2)—P—F(5) | 82.0 (7) |
| C(5)—C(6)—C(7) | 121.2 (10) | F(2)—P—F(6) | 96.3 (7) |
| C(6)—C(7)—C(8) | 121.7 (11) | F(3)—P—F(4) | 179.2 (6) |
| C(6)—C(7)—C(14) | 118.1 (12) | F(3)—P—F(5) | 87.9 (8) |
| C(8)—C(7)—C(14) | 120.2 (12) | F(3)—P—F(6) | 89.0 (8) |
| O(2)—C(8)—C(7) | 111.8 (11) | F(4)—P—F(5) | 91.3 (8) |
| O(2)—C(8)—C(9) | 122.7 (12) | F(4)—P—F(6) | 91.8 (8) |
| C(7)—C(8)—C(9) | 125.5 (13) | F(5)—P—F(6) | 176.5 (10) |
| S(1)—C(9)—C(8) | 123.6 (11) | | |

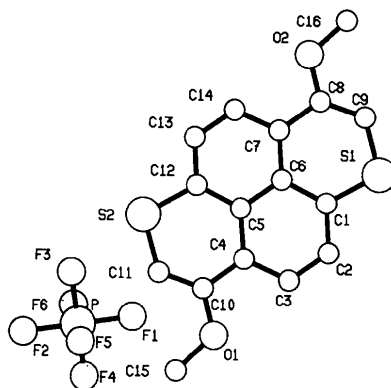


Fig. 1. Constituents with atomic numbering.

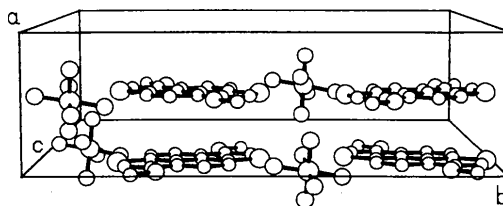


Fig. 2. Side view of stacks (tilted 5°). For clarity only one half on the unit-cell contents is shown.

observation has recently been made in the structure of a 3,8-diethyl-5,10-dimethyl-1,6-dioxapyrene complex with 7,7,8,8-tetracyano-*p*-quinodimethane (Thorup, Hjorth, Christensen & Bechgaard, 1992). The organic cations form segregated stacks (Fig. 2) along the short *a* axis, and two neighbouring cations are related by a glide operation ($x + \frac{1}{2}$, y , $\frac{1}{2} - z$). Interplanar distances are identical and equal to $\frac{1}{2}a = 3.314$ Å. The only S...S distance shorter than the van der Waals sum of 3.60 Å is a close S(1)...S(1) contact of 3.348 (2) Å between two neighbouring cations within the stack. The organic stacks are surrounded by PF₆⁻ anions. Some weak C—H...F interactions may exist, but a detailed analysis is hardly justifiable owing to the anion disorder.

Related literature. This work is part of a broad study of organic conducting materials. Owing to the small size of the present crystals the single-crystal conductivity was difficult to measure, but it was established that the crystals exhibit semiconducting activated behaviour with $\sigma(300\text{ K}) = 2.9\text{ S m}^{-1}$. Previously, we have studied a charge-transfer complex of 1,6-dithiapyrene with 7,7,8,8-tetracyano-*p*-quinodimethane (Thorup, Rindorf, Jacobsen, Bechgaard, Johannsen & Mortensen, 1985) with segregated stacks and metallic behaviour. In that compound the interplanar spacing of the cations was

3.39 Å, *i.e.* slightly longer than in the present structure. A number of 2,7-substituted 1,6-dithiapyrene compounds have been studied by Nakasuji and co-workers (Nakasuji, Sasaki, Kotani, Murata, Enoki, Imaeda, Inokuchi, Kawamoto & Tanaka, 1987; Kawamoto, Tanaka, Oda, Mizumura, Murata & Nakasuji, 1990).

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References

- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KAWAMOTO, A., TANAKA, J., ODA, A., MIZUMURA, H., MURATA, I. & NAKASUJI, K. (1990). *Bull. Chem. Soc. Jpn.*, **63**, 2137–2145.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NAKASUJI, K., SASAKI, M., KOTANI, T., MURATA, I., ENOKI, T., IMAEDA, K., INOKUCHI, H., KAWAMOTO, A. & TANAKA, J. (1987). *J. Am. Chem. Soc.* **109**, 6970–6975.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- SPEK, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- THORUP, N., HJORTH, M., CHRISTENSEN, J. B. & BECHGAARD, K. (1992). *Acta Cryst.* **C48**, 530–533.
- THORUP, N., RINDORF, G., JACOBSEN, C. S., BECHGAARD, K., JOHANNSEN, I. & MORTENSEN, K. (1985). *Mol. Cryst. Liq. Cryst.* **120**, 349–352.

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(5 α ,6 α ,7 α ,11 β)- $\Delta^{13,14}$ -Sophocarpine Monohydrate

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Abstract. 13,14-Didehydromatridin-15-one, C₁₅H₂₂N₂O.H₂O, *M_r* = 264.37, orthorhombic, *P*2₁2₁2₁, *a* = 10.667 (2), *b* = 16.552 (5), *c* = 8.116 (1) Å, *V* = 1433.0 (6) Å³, *Z* = 4, *D_x* = 1.225 g cm⁻³, Mo *K* α ₁, λ = 0.71069 Å, μ = 0.761 cm⁻¹, *F*(000) = 576, *T* = 294 K, *R* = 0.062 for 850 reflections [*I* > 3 σ (*I*)]. The

matrine-type alkaloid, isolated from the epigeal part of *Sophora nuttalliana* (syn. *sericea*) displays the 5 α ,6 α ,7 α ,11 β stereochemistry reported for (–)-sophocarpine. Rings *A*, *B* and *C* are in chair conformation. The water molecule is hydrogen bonded to the carbonyl O atom.