

$wR = 0.071$   
 $S = 1.617$   
 1821 reflections  
 209 parameters  
 H-atom parameters not refined  
 $w = 4F_o^2 / [\sigma(F)^2 + (0.07|F_o|^2)^2]$   
 $(\Delta/\sigma)_{\max} = 0.09$

Extinction correction:  
 $|F_c|(1 + gI_c)^{-1}$   
 Extinction coefficient:  
 $g = 1.6287 \times 10^{-7}$   
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Data collection: Enraf-Nonius CAD-4 software (Enraf-Nonius, 1985). Cell refinement: Enraf-Nonius software. Data reduction: Enraf-Nonius *SDP* (Frenz, 1985). Program(s) used to solve structures: Enraf-Nonius *SDP*. Program(s) used to refine structures: Enraf-Nonius *SDP*. Software used to prepare material for publication: Enraf-Nonius *SDP*. Absorption correction was performed using the *DIFABS* procedure (Walker & Stuart, 1983). The structures were solved by direct methods and successive difference Fourier syntheses. H atoms were placed in computed positions ( $C-H = 1 \text{ \AA}$ ,  $B_{eq} = 4 \text{ \AA}^2$ ). All calculations were performed on a MicroVAX 3100 using the *SDP* programs.

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for (2)

$$B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$
Se1	0.6690 (1)	0.3465 (1)	0.3014 (1)	2.99 (2)
Se2	0.3638 (1)	0.6108 (1)	0.2748 (1)	3.36 (2)
S1	0.4882 (2)	0.1941 (2)	0.5592 (2)	2.53 (5)
S2	0.2103 (2)	0.4406 (3)	0.5299 (3)	3.02 (5)
C1	0.3977 (9)	0.3612 (9)	0.4721 (9)	2.5 (2)
C2	0.4689 (9)	0.4302 (9)	0.364 (1)	2.9 (2)
C3	0.6569 (9)	0.496 (1)	0.156 (1)	3.0 (2)
C4	0.527 (1)	0.609 (1)	0.1451 (9)	3.2 (2)
C5	0.1987 (9)	0.2960 (9)	0.6492 (9)	2.8 (2)
C6	0.3322 (9)	0.1816 (9)	0.665 (1)	2.8 (2)
C7	0.343 (1)	0.044 (1)	0.761 (1)	3.7 (2)
C8	0.190 (1)	0.041 (1)	0.804 (1)	5.1 (3)
C9	0.068 (1)	0.180 (1)	0.831 (1)	5.6 (3)
C10	0.051 (1)	0.300 (1)	0.720 (1)	4.0 (3)
C11	0.803 (1)	0.476 (1)	0.061 (1)	5.1 (3)
C12	0.493 (1)	0.735 (1)	0.034 (1)	3.9 (2)
P	0.1570 (3)	0.1430 (3)	0.2747 (3)	3.74 (6)
F1	0.0210 (8)	0.161 (1)	0.199 (1)	9.6 (3)
F2	0.2880 (9)	0.1271 (9)	0.354 (1)	12.1 (3)
F3	0.263 (1)	0.090 (1)	0.148 (1)	16.2 (4)
F4	0.173 (1)	-0.0180 (9)	0.311 (1)	15.3 (4)
F5	0.045 (1)	0.205 (2)	0.392 (1)	15.7 (5)
F6	0.145 (1)	0.298 (1)	0.219 (2)	16.9 (4)

Table 4. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (2)

Se1—C2	1.844 (8)	C5—C6	1.37 (1)
Se1—C3	1.880 (9)	C5—C10	1.48 (1)
Se2—C2	1.853 (8)	C6—C7	1.51 (1)
Se2—C4	1.868 (9)	C7—C8	1.49 (2)
S1—C1	1.715 (7)	C8—C9	1.46 (1)
S1—C6	1.729 (9)	C9—C10	1.47 (2)
S2—C1	1.725 (8)	P—F1	1.56 (1)
S2—C5	1.729 (9)	P—F2	1.55 (1)
C1—C2	1.40 (1)	P—F3	1.51 (1)
C3—C4	1.34 (1)	P—F4	1.51 (1)
C3—C11	1.53 (1)	P—F5	1.48 (1)
C4—C12	1.50 (1)	P—F6	1.50 (1)
C2—Se1—C3	92.9 (4)	C5—C6—C7	122.4 (8)
C2—Se2—C4	93.4 (4)	C6—C7—C8	108.9 (7)
C1—S1—C6	96.3 (4)	C7—C8—C9	119. (1)
C1—S2—C5	97.2 (4)	C8—C9—C10	115. (1)
S1—C1—S2	114.3 (5)	C5—C10—C9	110.9 (8)
S1—C1—C2	123.5 (6)	F1—P—F2	178.2 (5)
S2—C1—C2	122.2 (5)	F1—P—F3	90.3 (6)
Se1—C2—Se2	116.1 (5)	F1—P—F4	87.7 (6)
Se1—C2—C1	122.7 (5)	F1—P—F5	86.3 (6)
Se2—C2—C1	121.1 (5)	F1—P—F6	88.9 (7)
Se1—C3—C4	119.1 (7)	F2—P—F3	91.5 (6)
Se1—C3—C11	115.0 (6)	F2—P—F4	92.5 (6)
C4—C3—C11	125.9 (8)	F2—P—F5	91.9 (6)
Se2—C4—C3	118.3 (7)	F2—P—F6	91.2 (7)
Se2—C4—C12	114.4 (6)	F3—P—F4	85.7 (7)
C3—C4—C12	127.3 (8)	F3—P—F5	175.2 (6)
S2—C5—C6	114.9 (7)	F3—P—F6	87.5 (7)
S2—C5—C10	119.7 (6)	F4—P—F5	97.5 (8)
C6—C5—C10	125.4 (8)	F4—P—F6	172.4 (8)
S1—C6—C5	117.1 (7)	F5—P—F6	89.1 (8)
S1—C6—C7	120.3 (6)		

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55933 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1033]

## References

- Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.  
 Frenz, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.  
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1993). **C49**, 1189–1192

## Structure of Anthracenediylidene-bis-(1,3-dithiole)-Tetracyanoquinodimethane-Bis(cyanoformyl)phenyl-malononitrile Ylide Monohydrate: (Ext-TTF<sup>2+</sup>).TCNQ.(Y<sup>-</sup>)<sub>2</sub>.(H<sub>2</sub>O)

SMAÏL TRIKI AND LAHCÈNE OUAHAB\*

*Laboratoire de Chimie du Solide et Inorganique Moleculaire, URA 1495 CNRS, Université de Rennes I, 35042 Rennes CEDEX, France*

DOMINIQUE LORCY AND ALBERT ROBERT\*

*Laboratoire de Physicochimie Structurale, URA CNRS 704, Campus de Beaulieu, 35042 Rennes CEDEX, France*

(Received 1 October 1992; accepted 18 December 1992)

## Abstract

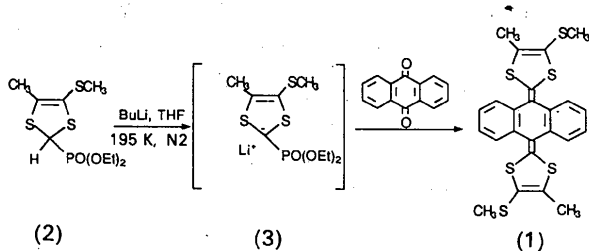
The crystal structure of the title compound is built from four kinds of molecule: one 7,7,8,8-tetracyano-*p*-quinodimethane [TCNQ: 2,2'-(2,5-cyclohexadiene-

1,4-diylidene)bispropanedinitrile]; two 2-[4-(cyanoformyl)phenyl]malononitrile ylides [ $Y^-$ : 2-[4-(cyanoformyl)phenyl]propanedinitrile ylide]; one extended 2,2',5,5'-tetrathiafulvalenium derivative [Ext-TTF<sup>2+</sup>: 2,2'-(9,10-anthracenediylidene)-5,5'-dimethyl-4,4'-bis(methylthio)bis(1,3-dithiole) cation] and one water molecule. The Ext-TTF<sup>2+</sup> is not planar; the dihedral angle between the planar anthracene group and the two dithiolium rings is 92°; this dication forms chains of monomers along the *a* axis. The TCNQ and the  $Y^-$  stack along the *b* axis. The inter-planar contact between the TCNQ molecule and the  $Y^-$  anion [3.31 (1) Å] is shorter than the one observed between two  $Y^-$  anions [3.47 (1) Å].

### Comment

The synthesis of the tetrathiafulvalene derivative (1) was achieved starting from phosphonate (2) (Bryce, Moore, Lorcy, Dhindsa & Robert, 1990). Ylide (3) was generated with BuLi and trapped by anthraquinone (1/2 equiv.) to yield (1) (80% yield) (Bryce & Moore, 1988).

The title compound was prepared by mixing hot acetonitrile solutions of 2 mmol TCNQ and 2 mmol of (1). On cooling to room temperature two types of black crystals were obtained (needles and parallelepipeds). A parallelepiped crystal suitable for X-ray structure determination was isolated from this batch.



(2)

(3)

(1)

The mechanism of the formation of  $Y^-$  (See molecule *A*, Fig. 1) from TCNQ<sup>2-</sup> in the presence of oxygen, has been described by Van Duyne and co-workers (Suchanski & Van Duyne, 1976). In fact, the electrochemical behaviour of Ext-TTF (1) is the same

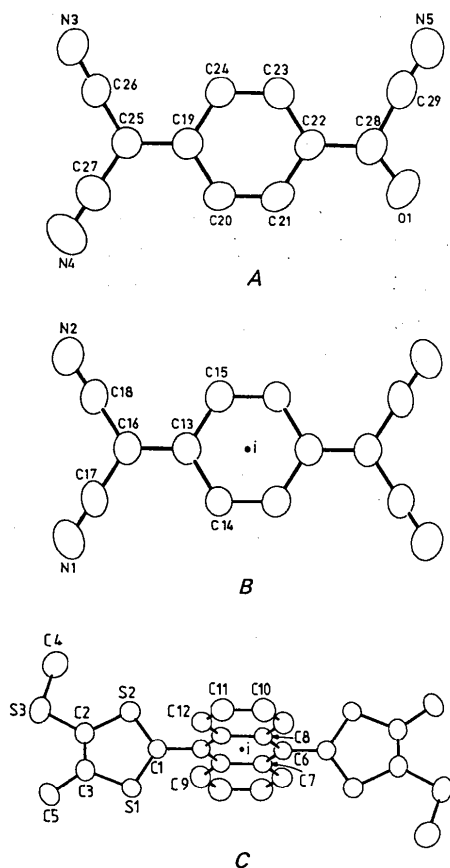


Fig. 1. Constituent molecules, *A* ( $Y^-$ ), *B* (TCNQ) and *C* (Ext-TTF<sup>2+</sup>), of the title compound with atom labelling.

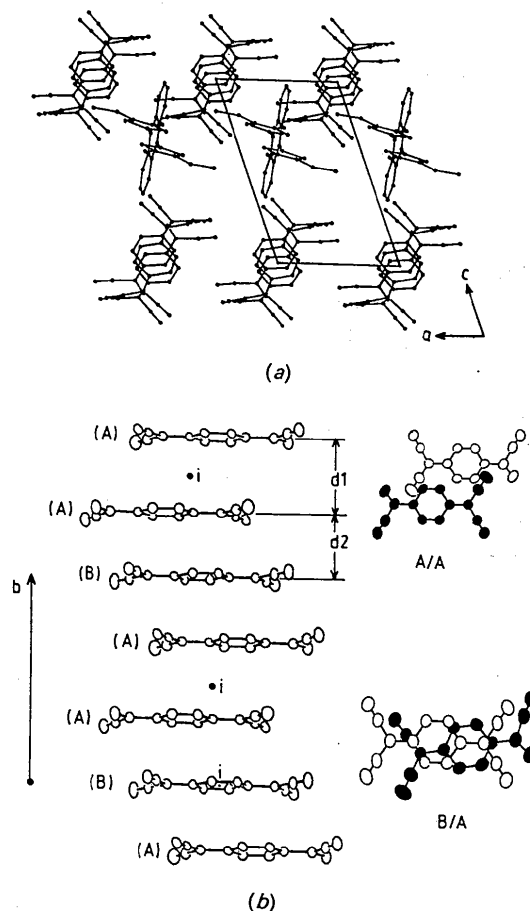


Fig. 2. (a) View of the crystal structure. (b) View of the anionic chains showing the different overlaps and the interplanar contacts [*d*1 = 3.47 (1), *d*2 = 3.31 (1) Å].

as that observed by Bryce, Moore, Masihul, Ashwell, Fraser, Clegg, Hursthouse & Karaulov (1990). The two-electron oxidation process which occurs at the same potential is not reversible. The presence of this dication favours the formation of TCNQ<sup>2-</sup>.

The crystal structure (Fig. 2*a*) is built from four kinds of molecule: one TCNQ (*B*), two Y<sup>-</sup> (*A*), one Ext-TTF<sup>2+</sup> (*C*) and one water molecule (Fig. 1). The Ext-TTF<sup>2+</sup> is not planar; the dihedral angle between the planar anthracene group and the two dithiole rings is 92° (see molecule *C*, Fig. 1). The central C—C length of 1.484 (5) Å is longer than those of 1.404 (14) and 1.38 (2) Å observed respectively in TTF<sup>+</sup> (Yakushi, Nishimura, Sugano & Kuroda 1980) and TMTTF<sup>+</sup> (Triki, Ouahab, Grandjean & Fabre, 1991). The dication Ext-TTF<sup>2+</sup> is located on a centre of symmetry and forms chains of monomers along the *a* axis (Fig. 2*a*). The TCNQ and the Y<sup>-</sup> anion stack along the *b* axis. The TCNQ molecule is located on the origin between two Y<sup>-</sup> anions. The stack is not regular; the inter-planar contact between the TCNQ molecule *B* and the Y<sup>-</sup> anion *A* [3.31 (1) Å] is shorter than that observed between two Y<sup>-</sup> anions [3.47 (1) Å] (Fig. 2*b*). The anionic sublattice can be described as formed by a succession of centrosymmetric trimers (*A/B/A*) along the *b* direction (Fig. 2*b*). The intra-trimer overlaps are of the bond-over-ring type (*A/B*), while the one between trimers (*A/A*) is shifted.

## Experimental

### Crystal data

C<sub>24</sub>H<sub>20</sub>S<sub>6</sub>.2(C<sub>11</sub>H<sub>4</sub>N<sub>3</sub>O).-

C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>.H<sub>2</sub>O

*M<sub>r</sub>* = 1111.37

Triclinic

*P* $\bar{1}$

*a* = 10.500 (2) Å

*b* = 11.110 (3) Å

*c* = 12.776 (2) Å

$\alpha$  = 72.66 (3)°

$\beta$  = 72.12 (2)°

$\gamma$  = 73.40 (3)°

*V* = 1322.5 Å<sup>3</sup>

*Z* = 1

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\theta$ -2 $\theta$  scans

Absorption correction:

empirical (*DIFABS*;

Walker & Stuart, 1983)

*T<sub>min</sub>* = 0.574, *T<sub>max</sub>* =

1.195

4931 measured reflections

4375 independent reflections

*D<sub>x</sub>* = 1.395 Mg m<sup>-3</sup>

Mo K $\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25 reflections

$\theta$  = 14–26°

$\mu$  = 0.3017 mm<sup>-1</sup>

*T* = 293 K

Parallelepiped

0.3 × 0.3 × 0.2 mm

Black

Crystal source: redox reaction in acetonitrile

2919 observed reflections

[*I* > 3 $\sigma$ ]

*R<sub>int</sub>* = 0.018

$\theta_{\max}$  = 25°

*h* = 0 → 12

*k* = -13 → 13

*l* = -15 → 15

3 standard reflections

frequency: 60 min

intensity variation: < 1%

### Refinement

Refinement on *F*

Final *R* = 0.050

*wR* = 0.066

*S* = 1.769

2919 reflections

353 parameters

H-atom parameters not refined

*w* = 4*F<sub>o</sub>*<sup>2</sup>/[ $\sigma(I)^2 + (0.06F_o^2)^2$ ]

( $\Delta/\sigma$ )<sub>max</sub> = 0.01

$\Delta\rho_{\max}$  = 0.361 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.094 e Å<sup>-3</sup>

Extinction correction:

|*F<sub>c</sub>*|(1 + *g**l*)<sup>-1</sup>

Extinction coefficient:

*g* = 8.575 × 10<sup>-7</sup>

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

	$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$			<i>B<sub>eq</sub></i>
	<i>x</i>	<i>y</i>	<i>z</i>	
Ext-TTF <sup>2+</sup> ( <i>C</i> )				
S1	-0.10356 (7)	0.15876 (7)	0.57600 (7)	3.43 (2)
S2	-0.28729 (8)	0.35012 (8)	0.46125 (8)	4.41 (2)
S3	-0.45404 (9)	0.1598 (1)	0.4780 (1)	6.91 (3)
C1	-0.1483 (3)	0.3133 (3)	0.5113 (2)	3.23 (7)
C2	-0.3208 (3)	0.1979 (3)	0.5054 (3)	3.65 (7)
C3	-0.2324 (3)	0.1059 (3)	0.5606 (2)	3.26 (7)
C4	-0.5383 (4)	0.3097 (5)	0.4095 (4)	8.0 (1)
C5	-0.2394 (3)	-0.0340 (3)	0.6043 (3)	4.19 (8)
C6	-0.0716 (3)	0.4102 (3)	0.5036 (2)	3.23 (6)
C7	0.0340 (3)	0.4385 (3)	0.4095 (2)	3.04 (6)
C8	0.1083 (3)	0.5305 (3)	0.4049 (2)	3.11 (6)
C9	0.2161 (3)	0.5585 (3)	0.3078 (3)	4.13 (8)
C10	0.2506 (4)	0.4986 (3)	0.2225 (3)	4.74 (9)
C11	0.1795 (4)	0.4059 (2)	0.2273 (3)	4.52 (8)
C12	0.0748 (3)	0.3769 (3)	0.3166 (3)	3.83 (7)
TCNQ ( <i>B</i> )				
N1	0.4597 (4)	-0.0764 (4)	-0.1931 (4)	8.3 (1)
N2	0.1738 (3)	0.2078 (4)	-0.3741 (3)	6.6 (1)
C13	0.1079 (3)	0.0223 (3)	-0.0971 (3)	3.90 (7)
C14	0.1338 (3)	-0.0692 (3)	0.0055 (3)	4.07 (8)
C15	-0.0315 (3)	0.0901 (3)	-0.0967 (3)	4.21 (8)
C16	0.2127 (3)	0.0449 (3)	-0.1907 (3)	4.17 (8)
C17	0.3503 (4)	-0.0225 (4)	-0.1931 (3)	5.5 (1)
C18	0.1913 (3)	0.1350 (4)	-0.2927 (3)	4.81 (9)
Y <sup>-</sup> ( <i>A</i> )				
N3	0.0648 (3)	0.8949 (3)	-0.3125 (2)	5.29 (8)
N4	0.3028 (4)	0.6013 (5)	-0.0928 (4)	8.7 (1)
N5	-0.6501 (4)	0.8549 (4)	0.1772 (3)	7.2 (1)
O1	-0.4329 (3)	0.6274 (3)	0.3105 (3)	7.6 (1)
C19	-0.0515 (3)	0.7290 (3)	-0.0386 (3)	3.84 (7)
C20	-0.0527 (4)	0.6425 (4)	0.0684 (3)	4.65 (9)
C21	-0.1704 (4)	0.6338 (4)	0.1489 (3)	5.0 (1)
C22	-0.2974 (3)	0.7126 (3)	0.1306 (3)	4.12 (8)
C23	-0.2976 (3)	0.7978 (3)	0.0252 (3)	4.14 (8)
C24	-0.1795 (3)	0.8080 (3)	-0.0564 (3)	3.86 (8)
C25	0.0715 (3)	0.7388 (3)	-0.1228 (3)	4.14 (8)
C26	0.0698 (3)	0.8249 (3)	-0.2284 (3)	3.98 (8)
C27	0.1995 (4)	0.6636 (4)	-0.1071 (3)	5.6 (1)
C28	-0.4207 (4)	0.7010 (4)	0.2170 (3)	5.2 (1)
C29	-0.5491 (4)	0.7892 (4)	0.1899 (3)	5.5 (1)
Water				
O2	0.5032 (8)	0.6272 (9)	0.0147 (3)	11.5 (3)

Table 2. Geometric parameters (Å, °)

S1—C1	1.668 (3)	C13—C15	1.442 (4)
S1—C3	1.703 (4)	C13—C16	1.370 (4)
S2—C1	1.668 (3)	C14—C15	1.334 (4)
S2—C2	1.718 (3)	C16—C17	1.420 (5)
S3—C2	1.727 (4)	C16—C18	1.422 (4)
S3—C4	1.757 (4)	N3—C26	1.129 (4)

C1—C6	1.484 (5)	N4—C27	1.143 (5)
C2—C3	1.354 (4)	N5—C29	1.130 (5)
C3—C5	1.502 (4)	O1—C28	1.223 (4)
C6—C7	1.389 (3)	C19—C20	1.417 (4)
C6—C8	1.410 (5)	C19—C24	1.422 (4)
C7—C8	1.431 (5)	C19—C25	1.412 (4)
C7—C12	1.437 (5)	C20—C21	1.350 (5)
C8—C9	1.423 (4)	C21—C22	1.415 (5)
C9—C10	1.347 (6)	C22—C23	1.397 (4)
C10—C11	1.412 (6)	C22—C28	1.429 (4)
C11—C12	1.352 (4)	C23—C24	1.361 (4)
N1—C17	1.133 (5)	C25—C26	1.403 (4)
N2—C18	1.141 (5)	C25—C27	1.403 (5)
C13—C14	1.446 (4)	C28—C29	1.492 (5)
C1—S1—C3	97.6 (2)	C15—C13—C16	121.2 (3)
C1—S2—C2	96.7 (2)	C13—C14—C15	120.7 (3)
C2—S3—C4	103.1 (2)	C13—C15—C14	121.5 (3)
S1—C1—S2	115.1 (2)	C13—C16—C17	122.0 (3)
S1—C1—C6	121.6 (2)	C13—C16—C18	122.6 (3)
S2—C1—C6	123.3 (2)	C17—C16—C18	115.5 (3)
S2—C2—S3	123.3 (2)	N1—C17—C16	178.9 (4)
S2—C2—C3	115.7 (3)	N2—C18—C16	179.6 (4)
S3—C2—C3	120.9 (3)	C20—C19—C24	116.9 (3)
S1—C3—C2	114.8 (2)	C20—C19—C25	121.6 (3)
S1—C3—C5	120.0 (2)	C24—C19—C25	121.5 (3)
C2—C3—C5	125.1 (3)	C19—C20—C21	121.4 (3)
C1—C6—C7	120.3 (3)	C20—C21—C22	121.4 (3)
C1—C6—C8	117.7 (2)	C21—C22—C23	117.7 (3)
C7—C6—C8	122.0 (3)	C21—C22—C28	120.3 (3)
C6—C7—C8	119.3 (3)	C23—C22—C28	122.0 (3)
C6—C7—C12	122.7 (3)	C22—C23—C24	121.5 (3)
C8—C7—C12	118.0 (2)	C19—C24—C23	121.1 (3)
C6—C8—C7	118.7 (2)	C19—C25—C26	120.5 (3)
C6—C8—C9	122.7 (3)	C19—C25—C27	122.8 (3)
C7—C8—C9	118.5 (3)	C26—C25—C27	116.8 (3)
C8—C9—C10	121.5 (4)	N3—C26—C25	178.2 (3)
C9—C10—C11	120.4 (3)	N4—C27—C25	179.0 (4)
C10—C11—C12	120.8 (4)	O1—C28—C22	127.5 (3)
C7—C12—C11	120.8 (3)	O1—C28—C29	116.4 (3)
C14—C13—C15	117.7 (2)	C22—C28—C29	116.2 (3)
C14—C13—C16	121.0 (3)	N5—C29—C28	175.2 (4)

The structure was solved by direct methods and successive difference Fourier syntheses. Full-matrix least-squares anisotropic ( $\beta_j$ ) refinement was performed on  $F_o$ . H atoms were included in the structure-factor calculations [ $C-H = 1 \text{ \AA}$ ,  $B = 5 \text{ \AA}^3$ ]. All calculations were performed on a MicroVAX 3100 computer using the *SDP* programs (B. A. Frenz & Associates, Inc., 1985).

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55936 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1032]

## References

- B. A. Frenz & Associates, Inc. (1985). *SDP Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- Bryce, M. R. & Moore, A. J. (1988). *Synth. Met.* **25**, 203–205.
- Bryce, M. R., Moore, A. J., Lorcy, D., Dhindsa, A. S. & Robert, A. (1990). *J. Chem. Soc. Chem. Commun.* pp. 470–472.
- Bryce, M. R., Moore, A. J., Masihul, H., Ashwell, G. J., Fraser, A. T., Clegg, W., Hursthouse, M. B. & Karaulov, A. I. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 1450–1452.
- Suchanski, M. R. & Van Duyne, R. P. (1976). *J. Am. Chem. Soc.* **98**, 250–252.
- Triki, S., Ouahab, L., Grandjean, D. & Fabre, J. M. (1991). *Acta Cryst.* **C47**, 1371–1373.

- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
- Yakushi, K., Nishimura, S., Sugano, T. & Kuroda, H. (1980). *Acta Cryst.* **B36**, 358–363.

*Acta Cryst.* (1993). **C49**, 1192–1195

## Structures of the 1:1 and 2:1 Adducts of (+)-(S)-[2.2]Paracyclophane-4-carboxylic Acid and (–)-Ephedrine

PETER G. JONES AND DETLEV DÖRING

*Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany*

THOMAS LAUE AND HENNING HOPF

*Institut für Organische Chemie der Technischen Universität, Hagenring 30, W-3300 Braunschweig, Germany*

(Received 22 June 1992; accepted 23 December 1992)

## Abstract

(+)-(S)-[2.2]Paracyclophane-4-carboxylic acid forms two adducts with (–)-ephedrine { $\alpha$ -[1-(methylamino)ethyl]benzenemethanol}. The 1:1 adduct, (–)-[1-( $\alpha$ -hydroxybenzyl)ethyl]methylammonium tricyclo[8.2.2.2<sup>4,7</sup>]hexadeca-4,6,10,12,13,15-hexaene-5-carboxylate, is an ephedrinium carboxylate, whereas the 2:1 adduct contains an additional undissociated carboxylic acid molecule. Both adducts are stabilized by extensive systems of hydrogen bonding, with contacts as short as 2.57 Å, which connect the residues into helices.

## Comment

Substituted cyclophanes are chiral molecules. The first resolution of enantiomers was performed by Cram & Allinger (1955) with the brucine salt of [2.2]paracyclophane-4-carboxylic acid. Absolute configurations for this acid were established by Falk, Reich-Rohrwig & Schlögl (1970) and confirmed by X-ray analysis of a camphorate derivative by Tochtermann *et al.* (1987).

Since [2.2]paracyclophane derivatives racemize only under the most extreme conditions (Cram & Reich, 1969; Cram & Delton, 1970), it should be possible to use enantiomerically pure [2.2]paracyclophanes to separate enantiomers of racemic amines. However, attempts to resolve ( $\pm$ )-ephedrine with (+)-(S)-[2.2]paracyclophane-4-carboxylic acid (1)