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X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

X. The Crystal Structure of Dithieno[1,2-*b*:5,4-*b'*]tropylium Tetrafluoroborate at 143 and 295 K

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(Received 27 October 1978; accepted 6 February 1979)

Abstract

(C₁₁H₇S₂)⁺BF₄⁻ is triclinic, space group *P* $\bar{1}$, with $a = 7.1949$ (12), $b = 8.7203$ (12), $c = 9.5967$ (20) Å, $\alpha = 105.787$ (15), $\beta = 99.074$ (13), $\gamma = 96.817$ (13)° at 143 K, $Z = 2$. The structure was refined to an *R* of 0.043 for 1448 non-zero counter reflexions at 143 K. The cation is almost planar; the angle between the planes of the two thiophene rings is 175.3 (4)°. Aromatic character is indicated by the relatively uniform C–C lengths. The S–C bonds are equal. The BF₄⁻ ion is disordered and has been described by two different orientations.

Introduction

The title compound is composed of dithienotropylium cations and BF₄⁻ anions. The cation has aromatic character and is relatively stable to hydrolysis. The chemical properties of tropylium ions substituted with thiophene rings have been studied by Yom-Tov (1972). The structure of one of these compounds of aromatic character, dithieno[2,1-*b*:4,5-*b'*]tropylium perchlorate, has been determined (Aurivillius, 1974) and the cation found to be planar.

The present compound (*E*.BF₄⁻, Fig. 1) is the first of a series (*E*,*A*,*B*), the structures of which have been determined. The second (*A*) is 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (Andersson, 1978) and the third (*B*) is 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (Andersson, 1975). Chemical and

spectroscopic data indicate a decrease of aromaticity from the first to the last compound, and the structures of *A* and *B* have been correlated with their chemical properties (Andersson, 1978). With the present structure determination the series will be completed.

The packing of the ions has been studied. The BF₄⁻ ions are disordered, which is also the case for ClO₄⁻ in the compound studied by Aurivillius (1974). The present structure was determined at both 143 and 295 K.

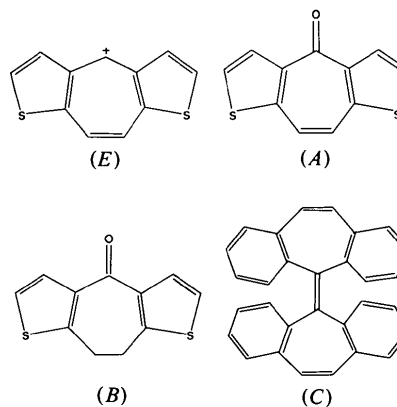


Fig. 1. Schematic drawings of the molecules: (*E*) dithieno[2,1-*b*:5,4-*b'*]tropylium tetrafluoroborate; (*A*) 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one; (*B*) 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one; (*C*) 2,3:6,7:2',3':6',7'-tetra-benzoheptafulvalene.

X-ray diffraction work

Only the experimental details at 143 K are given here. The experiment at 295 K was similar.*

A single crystal of $E.BF_4^-$ of regular form, and with a volume of $4.7 \times 10^{-3} \text{ mm}^3$, was used. Cell dimensions and intensities were determined on a four-circle diffractometer (Enraf-Nonius CAD-4) with equatorial geometry and Zr-filtered Mo K radiation ($\lambda = 0.71073 \text{ \AA}$). A flow of cold nitrogen gas was used to keep the crystal at 143 K (Danielsson, Grenthe & Oskarsson, 1976). Some crystal data are given in Table 1. The intensities of 2362 reflexions of which 910 had $I < 2\sigma_c(I)$ were measured (Lehmann & Larsen, 1974).*

Determination and refinement of the structure

The structure was solved from Weissenberg data by symbolic addition. The refinement was continued with diffractometer data* obtained at 295 K. A second crystal* and graphite-monochromatized Cu K radiation ($\lambda = 1.5418 \text{ \AA}$) were used. The final refinement was similar to the one at 143 K (*cf.* below). The temperature factors of the H atoms could not be refined and were given the value of 4.5 \AA^2 .* The resulting $R = 0.084$ and $R_w = 0.111$, $S = 1.45$.

The results of the room-temperature determination were used as a starting point for refinement with the low-temperature data.* The intensities were corrected

for Lorentz and polarization effects but not for absorption.

In the final full-matrix least-squares refinement of the 143 K data, the function minimized was $\sum w(\Delta|F|)^2$, where $\Delta|F| = |F_o| - |F_c|$. The weight function was $w^{-1} = \sigma_c^2(|F_o|) + 0.0016|F_o|^2 + 0.30$. Scattering factors were those of Doyle & Turner (1968) for non-hydrogen atoms, and for H those of Stewart, Davidson & Simpson (1965). The anomalous-scattering factors of Cromer & Liberman (1970) were used for non-hydrogen atoms. The BF_4^- ion was inserted in two different orientations, the occupancy factors (sum = 1) of which were refined relative to each other. Anisotropic temperature factors were refined,* except for F and H atoms, which were treated isotropically.

The final $R = \sum |\Delta|F| / \sum |F_o| = 0.043$ and $R_w = [\sum w(\Delta|F|)^2 / \sum w|F_o|^2]^{1/2} = 0.057$. The goodness of fit, $S = [\sum w(\Delta|F|)^2 / (m - n)]^{1/2} = 1.01$, where m is the number of observations and n the number of parameters. The final coordinates are given in Table 2.* A comparison of observed and calculated structure factors showed no apparent extinction. The residual electron density was < 0.67 and 0.28 e \AA^{-3} in the region of the BF_4^- and the tropylium ion respectively. The thermal parameters of the S and C atoms were explained as resulting from the motion of a rigid molecule (Schomaker & Trueblood, 1968). (No details of the calculations are given here.)

* See deposition footnote.

* Additional experimental and refinement details at 143 and 295 K, tables of positional parameters, least-squares planes and distances and angles involving H atoms and angles in the dithienotropylium ion at 295 K, lists of structure factors, thermal parameters, details of the crystal habit and distances and angles in the BF_4^- ion at 295 and 143 K and details of additional least-squares planes at 143 K, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34178 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Crystal data

| $(C_{11}H_7S_2)^+ BF_4^-$, FW 290.1, triclinic, space group $P\bar{1}$ | | |
|---|---|-----------------------|
| | 143 K | 295 K |
| a | 7.1949 (12) Å | 7.3124 (6) Å |
| b | 8.7203 (12) | 8.6753 (5) |
| c | 9.5967 (20) | 9.6675 (5) |
| α | 105.787 (15)° | 105.589 (4)° |
| β | 99.074 (13) | 98.794 (6) |
| γ | 96.817 (13) | 96.893 (7) |
| V | 563.82 Å ³ | 575.36 Å ³ |
| $Z = 2$ | $\mu(\text{Mo } K\alpha) = 0.48 \text{ mm}^{-1}$ (143 K) | |
| $D_m = 1.66 \text{ Mg m}^{-3}$ | $\lambda(\text{Mo } K\alpha_1) = 0.70930 \text{ \AA}$ (143 K) | |
| $D_x = 1.67$ | $\mu(\text{Cu } K\alpha) = 4.4 \text{ mm}^{-1}$ (295 K) | |
| | $\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$ (295 K) | |

Table 2. Positional and isotropic thermal parameters with *e.s.d.*'s in parentheses (143 K)

The expression for the isotropic temperature factor is $\exp[-8\pi^2 U (\sin^2 \theta / \lambda^2)]$.

| Occupancy | x | y | z | $8\pi^2 U (\text{Å}^2)$ |
|-----------|--------------|--------------|--------------|-------------------------|
| S(1) | 0.25351 (15) | 0.42078 (12) | 0.49981 (11) | |
| S(2) | 0.14294 (16) | 0.85026 (12) | 0.04346 (13) | |
| C(1) | 0.2438 (5) | 0.5132 (5) | 0.3608 (5) | |
| C(2) | 0.1955 (6) | 0.6696 (5) | 0.3897 (5) | |
| C(3) | 0.1725 (6) | 0.7607 (5) | 0.2933 (5) | |
| C(4) | 0.1885 (5) | 0.7178 (5) | 0.1442 (5) | |
| C(5) | 0.1900 (7) | 0.7229 (6) | -0.1136 (5) | |
| C(6) | 0.2393 (6) | 0.5855 (5) | -0.0951 (5) | |
| C(7) | 0.2412 (6) | 0.5750 (5) | 0.0532 (4) | |
| C(8) | 0.2893 (6) | 0.4417 (5) | 0.0959 (4) | |
| C(9) | 0.2918 (5) | 0.4115 (5) | 0.2323 (5) | |
| C(10) | 0.3419 (6) | 0.2629 (5) | 0.2573 (5) | |
| C(11) | 0.3254 (6) | 0.2535 (5) | 0.3930 (5) | |
| F(12) | 0.4112 (9) | 0.0141 (8) | 0.6349 (11) | 3.03 (14) |
| F(13) | 0.1160 (8) | -0.0292 (7) | 0.6985 (12) | 2.98 (14) |
| F(14) | 0.2538 (14) | 0.2206 (7) | 0.7128 (7) | 2.68 (13) |
| F(15) | 0.3787 (15) | 0.0924 (7) | 0.8772 (6) | 2.82 (14) |
| F(17) | 0.4319 (16) | -0.0037 (13) | 0.6740 (19) | 2.91 (25) |
| F(18) | 0.3214 (30) | 0.0900 (13) | 0.8823 (12) | 3.55 (25) |
| F(19) | 0.1188 (13) | 0.0352 (11) | 0.6599 (19) | 2.30 (22) |
| F(20) | 0.3047 (27) | 0.2292 (13) | 0.7181 (12) | 2.96 (24) |
| B | 0.2926 (7) | 0.0731 (6) | 0.7302 (5) | |
| H(2) | 0.186 (8) | 0.718 (7) | 0.486 (7) | 2.6 (10) |
| H(3) | 0.137 (6) | 0.859 (5) | 0.324 (5) | 1.0 (8) |
| H(5) | 0.170 (8) | 0.746 (7) | -0.202 (7) | 3.1 (11) |
| H(6) | 0.268 (8) | 0.504 (7) | -0.166 (6) | 2.9 (11) |
| H(8) | 0.325 (7) | 0.352 (6) | 0.017 (6) | 1.8 (9) |
| H(10) | 0.376 (7) | 0.199 (6) | 0.195 (6) | 1.6 (9) |
| H(11) | 0.350 (9) | 0.175 (8) | 0.436 (7) | 4.7 (15) |

A refinement in which anisotropic temperature factors were used only for the S atoms, but in other details similar to the final one, gave $R = 0.048$ and $R_w = 0.063$, $S = 1.09$. The residual electron density was $<0.66 e \text{ \AA}^{-3}$.

Discussion of the structure at 143 K

The compound is ionic, and composed of dithienotropylium cations (Fig. 2) and BF_4^- anions. The cation has no inherent crystallographic symmetry. The structure consists of planes of tilted tropylium ions at right angles to a with BF_4^- ions in the space between four tropylium ions (Fig. 3a). Parallel to the ac plane, layers of tropylium ions with layers of BF_4^- ions in between can be distinguished.

From crystallographic symmetry the best planes of the tropylium ions are all parallel (Fig. 3b), and within a layer the distance between the planes is 3.347 \AA . The planes of a neighbouring layer are 1.169 and 2.179 \AA from a tropylium ion plane. The shortest contacts between the tropylium ions are given in Table 3. Most of these contacts are within a layer.

The BF_4^- ion is disordered, with two predominant orientations. The shortest distances between BF_4^- ions (Table 3) are found in the approximate ac plane. Between the layers in the direction of these planes the distances are considerably greater.

The distances from the BF_4^- ions to the tropylium ions (Table 3) are short relative to the van der Waals distances and the distances between ions of the same charge.

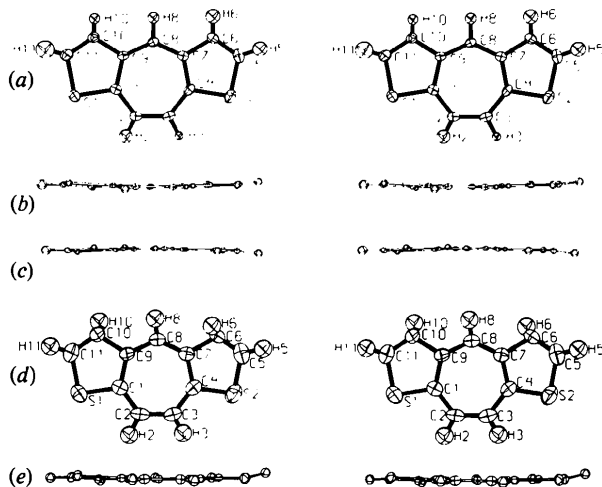


Fig. 2. A view of the cation E from three different directions and at two different temperatures; (a), (b), (c) at 143 K and (d), (e) at 295 K. In (a) and (d) 50% probability ellipsoids are shown, in (b) and (e) C(2) and C(3) point towards the reader and in (c) C(8) points towards the reader.

Table 3. Intermolecular distances (\AA) at 143 and 295 K

Van der Waals radii (Bondi, 1964) and upper limits at 143 and 295 K are given. This is followed by the atoms, the distance between them at 143 K and the increase in distance ($\times 10^3$) from 143 to 295 K. Distances between layers are marked with an asterisk.

| Distances between cations | | | Distances between anions | | |
|---------------------------|-----------|-------|----------------------------------|------------|-------|
| VdW 3.5 | <4.00 | <4.00 | VdW 3.0 | <3.90 | <3.83 |
| S(1)–S(1) | 3.650 (2) | 31 | F(12)–F(12) | 3.027 (18) | 110 |
| S(2)–S(2)* | 3.697 (2) | 72 | F(15)–F(15) | 3.554 (13) | 91 |
| VdW 3.45 | <3.69 | <3.71 | F(19)–F(19) | 3.513 (29) | >487 |
| S(1)–C(1) | 3.573 (4) | 89 | F(17)–F(17) | 3.640 (31) | >360 |
| S(2)–C(8) | 3.591 (4) | 18 | F(12)–F(17) | 3.317 (18) | 342 |
| S(2)–C(10)* | 3.611 (4) | 17 | F(13)–F(19) | 3.801 (18) | –398 |
| S(1)–C(2) | 3.621 (4) | 71 | F(15)–F(18) | 3.709 (16) | >291 |
| VdW 2.95 | <3.34 | <3.44 | Distances between different ions | | |
| S(1)–H(6) | 3.07 (6) | 570 | VdW 3.25 | <3.35 | <3.41 |
| S(2)–H(10)* | 3.13 (5) | 180 | F(14)–S(1) | 3.028 (6) | 45 |
| S(1)–H(2) | 3.29 (5) | –30 | F(20)–S(1) | 3.020 (10) | 153 |
| VdW 3.4 | <3.59 | <3.65 | F(18)–S(2) | 3.187 (12) | –70 |
| C(5)–C(9) | 3.428 (5) | 69 | F(18)–S(2) | 3.592 (20) | –338 |
| C(6)–C(8) | 3.429 (5) | 80 | VdW 3.2 | <3.20 | <3.23 |
| C(7)–C(7) | 3.447 (7) | 44 | F(12)–C(11) | 3.159 (7) | 13 |
| VdW 2.9 | <3.31 | <3.31 | F(14)–C(3) | 3.082 (10) | 93 |
| C(6)–H(8) | 3.05 (5) | 160 | F(17)–C(11) | 2.950 (11) | –11 |
| C(8)–H(6) | 3.10 (6) | 210 | F(17)–C(10) | 3.089 (12) | –158 |
| VdW 2.4 | <3.00 | <3.11 | VdW 2.7 | <2.41 | <2.47 |
| H(3)–H(11)* | 2.82 (8) | 48 | F(18)–H(8) | 2.30 (5) | 110 |
| H(2)–H(5) | 2.96 (8) | 100 | | | |

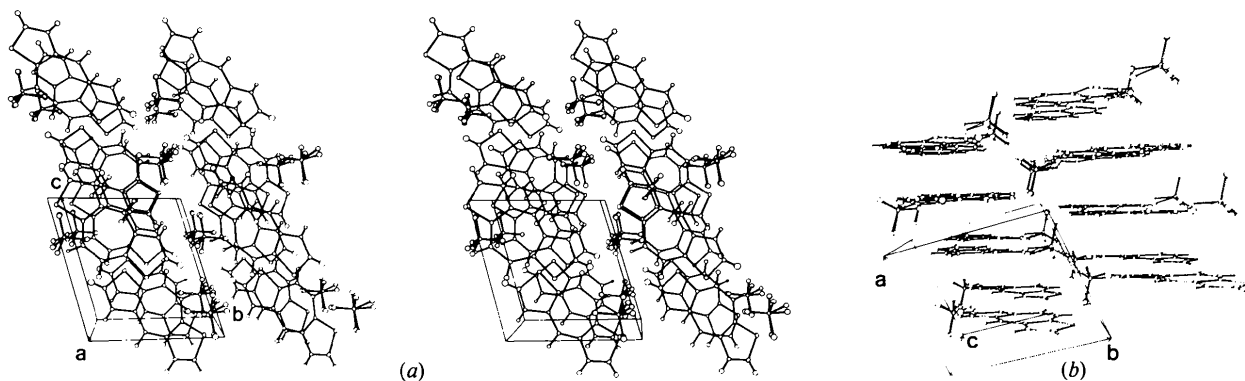


Fig. 3. (a) A stereoview of the stacking of ions E at 143 K with a pointing towards the reader. (b) A view of the stacking of ions E at 143 K with the planes of cations seen from the side.

Comparison with the structure at 295 K*

The thermal expansion of the unit cell is seen in Table 1. The cell volume increases by 2.05%. In the direction of *b*, approximately at a right angle to the tropylium ion layers, there is a decrease of the cell axis.

The distance between the best planes of tropylium ions in a layer increases from 3.347 to 3.378 Å.

There is a general rather uniform increase in the short contacts between tropylium ions (Table 3). Between tropylium ions and BF_4^- ions the increase is not so regular, and between BF_4^- ions there are large deviations from the general increase. This might be caused by differences in the orientations of the BF_4^- ions (*cf.* below).

* See deposition footnote.

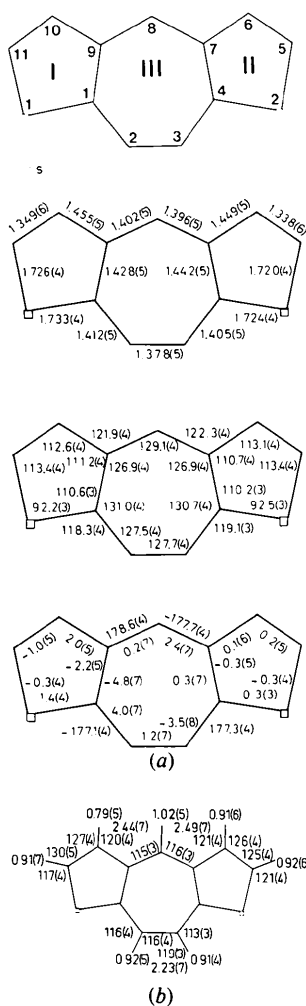


Fig. 4. (a) Schematic diagrams showing the non-hydrogen atoms of the dithienotropylium ion *E* at 143 K. The numbering of the ring system and the atoms, as well as selected distances (Å), bond angles ($^\circ$) and torsion angles ($^\circ$), is presented. The e.s.d.'s are given in parentheses. (b) Distances (Å) and angles ($^\circ$) involving H atoms.

The bond distances in the cation at 143 and 295 K are given in Figs. 4 and 5. With a few exceptions the distances are smaller at 295 than at 143 K. This is probably an apparent shortening due to thermal motion. The conformations of the cations are very similar (Fig. 2). The angle between planes I and II (Table 4) is $176.3(4)^\circ$ at 295 K compared to $175.3(4)^\circ$ at 143 K.

The BF_4^- ion also shows an apparent shortening of bond distances due to thermal motion.* The two orientations change slightly relative to each other with temperature. The mean of angles equivalent to $\text{F}(12)-\text{B}-\text{F}(17)$ (Table 2) is $32(1)^\circ$ at 295 K and $16.5(6)^\circ$ at 143 K.

The thermal parameters (Table 2, Fig. 2) are directly proportional to the absolute temperature for the F atoms as well as for the other atoms, which is an indication that the disorder is not drastically altered. Also at 295 K the method of Schomaker & Trueblood (1968) was successful in explaining the thermal motion. The thermal expansion and the apparent shortening mentioned above combine to give increased values of the short contacts with temperature.

* See deposition footnote.

Table 4. Least-squares planes (143 K)

Deviations ($\times 10^3$ Å) of the atoms from the planes (*cf.* Fig. 4), and the angles between them are given. Atoms used to define the planes are marked with asterisks. Weights proportional to the atomic numbers are used. The e.s.d.'s for the deviations of S, C and H atoms are 2, 5 and 60 ($\times 10^3$ Å) respectively. Details of additional least-squares planes have been deposited.

| | Plane I | Plane II | Plane III | | |
|--------|---------|----------|-----------|-------|-----|
| S(1)* | -3 | S(2)* | 1 | C(1)* | -31 |
| C(1)* | 13 | C(4)* | -2 | C(2)* | 6 |
| C(9)* | -13 | C(7)* | 1 | C(3)* | 24 |
| C(10)* | 7 | C(6)* | 1 | C(4)* | -15 |
| C(11)* | 1 | C(5)* | -2 | C(7)* | -16 |
| C(2) | 66 | C(3) | 5 | C(8)* | 18 |
| C(8) | -84 | C(8) | 7 | C(9)* | 14 |
| H(10) | 29 | H(6) | -11 | H(8) | 31 |
| H(11) | 28 | H(5) | -83 | H(2) | 86 |
| | | | | H(3) | 20 |

Angles ($^\circ$) between the planes

| | |
|--------|-----------|
| I-II | 175.3 (4) |
| I-III | 176.7 (7) |
| II-III | 178.4 (6) |

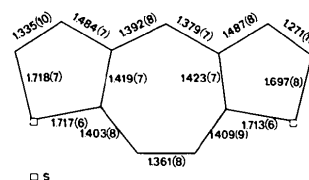


Fig. 5. The dithienotropylium ion *E* at 295 K. Distances (Å) are presented. The numbering of the ring system and the atoms is as in Fig. 4.

Conformation

The deviations of the atoms from the thiophene rings are significant for plane I but not for plane II. The atoms C(2) and C(8) in the cycloheptatrienylium ring deviate greatly from plane I, in contrast to the deviations of C(3) and C(8) from plane II. There is a minor twist of ring I. The seven-membered ring has a boat conformation distorted by a twist. The angle between planes I and II is 175.3 (4)°.

The statistical distribution of chemically equivalent bond distances and angles (Fig. 4a) in the cation indicates that the e.s.d.'s are overestimated by a factor of 0.7 and that systematic deviations occur (Hamilton, 1974). All distances on the left side except one are longer than the corresponding ones on the right and the same features are found at 295 K. The e.s.d.'s multiplied by a factor of 1.7 have been used when calculating mean values for Table 5.

Within each half of the cation the S—C bonds are not significantly different. The bond lengths of the central ring lie within a smaller interval than those of the thiophene rings. The formal single bonds C(1)—C(2), C(3)—C(4) and C(7)—C(8), C(8)—C(9) of the central ring are of about the same length. The angles differ only

slightly from the ideal values for five- and seven-membered rings. The H atoms* (Figs. 2, 4b) are not significantly out of their respective planes (Table 4).

The e.s.d.'s for the BF₄⁻ ion are underestimated by a factor of 2.2 and the mean B—F distance is 1.397 (8) Å.

Comparison with *A*

The structure of *A* (Fig. 1) was also determined at low temperature (173 K), and the precision is high with no apparent systematic deviations. A stereoview of *A* is given in Andersson (1978). The conformations of *E* and *A* are very much alike. *A* is slightly more bent than *E* and has an approximate mirror symmetry with a twist and both thiophene rings non-planar, in contrast to *E* for which ring II is planar. In both structures the seven-membered ring has a twisted-boat form. The angles between planes I and II are 175.3 (4)° for *E* and 171.6 (8)° for *A*.

Conformations and properties

E is the first in the series *E*, *A*, *B* of decreasing aromatic properties (Andersson, 1978). *E* and *A* are nearly planar and *B* has a twisted form.

The bond lengths are compared to those accepted for single and double bonds in Table 5. Another molecule (*C*), 2,3:6,7:2',3':6',7'-tetrabenzoheptafulvalene (Dichmann, Nyburg, Pickard & Potworowski, 1974), included in Table 5 and Fig. 1 for comparison, has the seven-membered rings in the boat form. The bond lengths of the central ring of *E* are closer to those of aromatic compounds and of graphite than those of the other compounds of the series, indicating a higher degree of conjugation. C(1)—C(9) and C(4)—C(7) are longer than the formal single bonds C(1)—C(2), C(3)—C(4) and C(7)—C(8), C(8)—C(9). The spread of the bond distances increases in a regular way through the series *E*, *A*, *B*. The C—C distances in the thiophene rings, in contrast, become more alike, and the S—C distances more different in the series. *C* is to be primarily compared to *A* as they have similar electronic structures.

The C(7)—C(8)—C(9) angle in *E* is much greater than in *A*, 129.1 (4)°, and the mean of the other angles in the central ring is 128.5°, indicating slightly less angular strain than in *A*, but much higher than that in *C*. The angles at the thiophene rings are smaller for *E* than for *A*. In the thiophene rings the angles at C(5), C(6) and C(10), C(11) are more alike in *E* than in *A*.

Intramolecular interactions are not large in *E*, and are mainly H—H and H—C interactions (Fig. 4b). In *C*

Table 5. Mean values of bond distances (Å)

The e.s.d.'s for *E*, *A* and *B* are multiplied by 1.7, 0.7 and 1.6, respectively (see text). Notation: *s* = single bond, *d* = double bond. The reference distances are taken from *International Tables for X-ray Crystallography* (1962) and from Kitaigorodsky (1973).

| Seven-membered ring | | | | |
|------------------------------------|--------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|
| Compound | C(2)—C(3) <i>d</i> or <i>s</i> | C(1)—C(9) C(4)—C(7) <i>d</i> | C(1)—C(2) C(3)—C(4) <i>s</i> | C(7)—C(8) C(8)—C(9) <i>s</i> |
| <i>E</i> (143 K) | 1.378 (5) | 1.435 (7) | 1.409 (7) | 1.399 (7) |
| <i>A</i> (173 K) | 1.352 (4) | 1.393 (3) | 1.425 (3) | 1.467 (3) |
| <i>B</i> (295 K) | 1.516 (12) | 1.373 (7) | 1.493 (8) | 1.479 (7) |
| <i>C</i> (ca 295 K, molecule 1) | 1.341 (5) | 1.406 (4) | 1.456 (4) | 1.489 (3) |
| Reference bonds | Double (simple) 1.337 (6) | Aromatic 1.395 (3) | Graphite 1.4210 (1) | Single (partial) 1.476 |
| | Single (partial) 1.507 | | | |
| Thiophene rings | | | | |
| Compound | C(10)—C(11) C(5)—C(6) <i>d</i> | C(9)—C(10) C(6)—C(7) <i>s</i> | | |
| <i>E</i> (143 K) | 1.344 (8) | 1.452 (7) | | |
| <i>A</i> (173 K) | 1.345 (4) | 1.426 (4) | | |
| <i>B</i> (295 K) | 1.340 (8) | 1.430 (8) | | |
| Compound | | S(1)—C(1) S(2)—C(4) <i>s</i> | S(1)—C(11) S(2)—C(5) <i>s</i> | |
| <i>E</i> (143 K) | | 1.729 (5) | 1.723 (5) | |
| <i>A</i> (173 K) | | 1.738 (3) | 1.716 (3) | |
| <i>B</i> (295 K) | | 1.722 (6) | 1.714 (7) | |

* See deposition footnote.

such interactions have been minimized by taking a boat form.

Thus, there is a gradual change in the detailed geometry throughout the molecules of the series in the crystalline state. This change in geometry parallels that of chemical properties.

The author thanks Professor Bengt Aurivillius for valuable discussions and Dr Åke Oskarsson for assistance with the low-temperature apparatus. This work received financial support from the Swedish Natural Science Research Council.

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The Crystal and Molecular Structure of 3-Carboxymethylthio-1,5-diphenylformazan

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(Received 1 December 1978; accepted 12 February 1979)

Abstract

$C_{15}H_{14}N_4O_2S$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 27.98$ (1), $b = 10.127$ (5), $c = 5.208$ (3) Å, $\beta = 91.59$ (5)°, $Z = 4$. The structure was refined to $R = 0.053$ for 965 observed reflections. The molecules are remarkably planar and are strongly hydrogen bonded through their carboxylic groups to form dimers ($O \cdots O = 2.66$ Å). The imino proton participates in a weak intramolecular hydrogen bond which stabilizes the N–N–C–N–N chain in a *syn,s-trans* configuration relative to the formal double C=N and single C–N bonds.

Introduction

3-Carboxymethylthio-1,5-diphenylformazan (3) is being studied as a potential terdentate ligand since it

incorporates the chromophoric groups of dithizone (1) (Irving, 1977) and *S*-methyldithizone (2) (Irving, Nabils & Sahota, 1973), and unlike the latter contains an acidic group which should facilitate the formation of metal chelates and lend itself to liquid–liquid extraction procedures. However, complete absence of the expected metal complexes, coupled with exceptional acid dissociation constants, unusual visible, IR and NMR spectroscopic properties and the existence of (3) as a monomer in solution, suggested a conformation in which the –OH group of the side chain points almost axially through the centre of the π -electron system of a quasi-aromatic formazan ring, as (5) (Hutton, Irving, Koch, Nassimbeni & Gafner, 1979). Although hydrogen bonding to π -electron systems is well established (Joesten & Schaad, 1974), there are few precedents for the novel structure (5) and an X-ray crystallographic investigation of (3) was undertaken to ascertain whether this molecular structure persisted in the solid state.

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