The Structure of the CT Complex Between 5,7,12,14-Tetramethoxydibenzo[*b,i*]thianthrene with TCNQ

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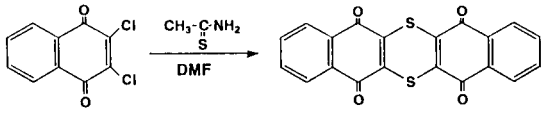
Received May 5, 1992

The structure of 1,4-dithiines obtained from orthodihalogeno heterocycles with thiocarbonyl compounds was determined by X-ray structure analysis of the intermolecular charge-transfer complex between 5,7,12,14-tetramethoxydibenzo[*b,i*]thianthrene and TCNQ. The formation of the thiazole ring has already been reported but the products were confirmed to be 1,4-dithiines by X-ray structure analysis and the previously reported results.

J. Heterocyclic Chem., **30**, 173 (1993).

The reactions of orthodihalogeno heterocycles with thiocarbonyl compounds gave the corresponding 1,4-dithiines [1,2] but not the previously reported thiazoles [3,4]. For example, the reaction of 2,3-dichloronaphthoquinone with thioacetoamide in dimethylformamide gave dibenzo-[*b,i*]thianthrene-5,7,12,14-tetrone **1** in 95% yield [2] (Scheme 1). The mismatch of the reaction products between dithiines and thiazoles was corrected in the previous papers [1,2] exemplifying many combinations of reactions. The identifications of products by elemental analyses and other spectral analyses were also conducted.

Scheme 1



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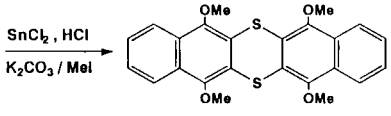

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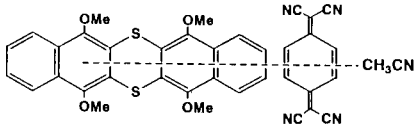
Scheme 2



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In this paper an X-ray structure determination of the intermolecular CT complex **3** between 5,7,12,14-tetramethoxydibenzo[*b,i*]thianthrene, **2**, and tetracyanoquinodimethane (TCNQ) [5] is described. The chemical composition of the CT complex **3**, shown in Scheme 2, was determined by elemental analyses [2] and the ratio of integral values in the ^{1}H-nmr spectra [6]: the component ratio was **2**/TCNQ/CH_3CN = 1:1:1. The crystal data is given in Table 1.

Table 1

Crystal Data of 3

Formula	$C_{24}H_{20}O_4S_2 \cdot C_{12}H_4N_4 \cdot CH_3CN$
Formula Weight	681.80
Crystal System	Orthorhombic
Space Group	Pnma
Cell Dimensions	
a/Å	14.027(2)
b/Å	13.675(2)
c/Å	17.352(2)
V/Å	3328.5(8)
Z	4
Dobs/g.cm^{-3}	1.378
D_{calcd}/g cm^{-3}	1.3606(3)

Single crystals were obtained from an acetonitrile solution by slow evaporation. A black columnar single-crystal of good quality in size of 0.81 x 0.47 x 0.59 mm^3 was selected for the X-ray analysis. The crystals belong to the orthorhombic space group of Pnma with four pairs of each component in the unit cell. The X-ray intensities were measured by ω-2θ scan technique using a four-circle automatic diffractometer with monochromated MoKα radiation. Altogether 5047 reflections were measured, of which 1881 reflections with $|Fo| > 3\sigma(Fo)$ were considered as observed and used for the structure determination. The structure was solved by the direct method using the program MULTAN 78 [7] and was refined by the least-squares method. All the hydrogen atoms, except those of acetonitrile, were found from a difference Fourier map and they were included in the least-squares calculation with a fixed isotropic thermal factor. The final residual index R was 0.083. The final atomic parameters are given in Table 2.

The molecular structures of **2** and TCNQ in complex **3** are illustrated in Figures 1 and 2, respectively. The moiety **2** is centrosymmetric: the center of symmetry, shown by a small circle, is located at the origin. Molecule **2** is some-

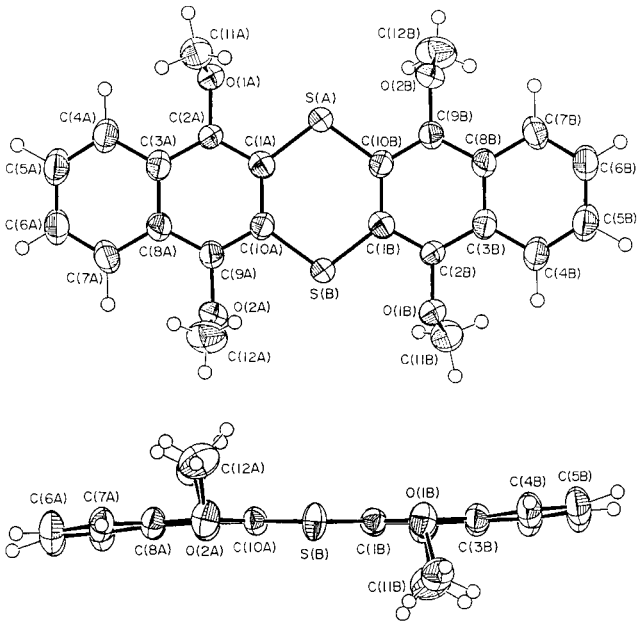

Figure 1. Molecular structure and atomic numbering scheme of 2 in the complex 3. Upper: viewed perpendicular to the molecular plane. Lower: viewed parallel to the molecular plan. Thermal ellipsoids for the non-hydrogen atoms are drawn at 50% probability level. Hydrogen atoms are shown by spheres of a fixed arbitratry radius. The atoms having labels A and B are related to each other by the center of symmetry located at the center of the molecule shown by the small circle.

Table 2

Final fractional atomic coordinates and equivalent isotropic temperature factors, B_{eq}, with e.s.d.'s in parentheses. Hydrogen atoms are assigned the same numbers as the heavy atoms to which they are bonded, and the thermal parameters are assumed to have a fixed value

Atom	x	y	z	B_{eq}/Å^2
(a) Tetramethoxydibenzo[*b*,*i*]thiathrene moiety, 2 (on the center of symmetry at the origin)				
S(A)	0.05137(9)	0.00866(12)	0.40750(7)	3.78(3)
O(1A)	0.2483(2)	0.0200(3)	0.4160(2)	3.7(1)
O(2A)	0.0887(2)	-0.0159(3)	0.7066(2)	4.1(1)
C(1A)	0.1119(3)	0.0053(4)	0.4957(3)	3.0(1)
C(2A)	0.2095(3)	0.0116(4)	0.4895(3)	3.0(1)
C(3A)	0.2711(4)	0.0138(4)	0.5540(3)	3.4(1)
C(4A)	0.3706(4)	0.0318(5)	0.5468(3)	4.4(2)
C(5A)	0.4259(4)	0.0359(5)	0.6124(4)	5.1(2)
C(6A)	0.3864(4)	0.0210(6)	0.6855(4)	5.4(2)
C(7A)	0.2894(4)	0.0032(5)	0.6945(3)	4.3(2)
C(8A)	0.2299(3)	0.0024(4)	0.6288(3)	3.5(1)
C(9A)	0.1300(3)	-0.0078(4)	0.6339(3)	3.2(1)
C(10A)	0.0709(3)	-0.0030(4)	0.5706(3)	3.1(1)
C(11A)	0.2899(4)	-0.0707(5)	0.3902(3)	4.6(2)
C(12A)	0.0870(5)	-0.1168(5)	0.7341(4)	5.9(2)
H(4A)	0.403(8)	0.050(9)	0.490(7)	7.0
H(5A)	0.501(8)	0.063(9)	0.609(6)	7.0
H(6A)	0.427(8)	0.022(9)	0.731(6)	7.0
H(7A)	0.257(8)	-0.001(8)	0.753(7)	7.0
H(11a)	0.329(8)	-0.053(9)	0.345(7)	7.0
H(11b)	0.335(8)	-0.101(9)	0.426(6)	7.0
H(11c)	0.245(8)	-0.118(9)	0.378(6)	7.0
H(12a)	0.148(8)	-0.148(8)	0.735(6)	7.0
H(12b)	0.067(8)	-0.117(9)	0.780(6)	7.0
H(12c)	0.056(8)	-0.170(9)	0.698(6)	7.0

Table 2 (continued)

Atom	x	y	z	B_{eq}/Å^2
(b) TCNQ (on the mirror plane at y = 1/4)				
C(1)	0.0646(6)	1/4	0.4945(5)	3.9(2)
C(2)	0.0161(6)	1/4	0.5606(5)	3.9(2)
C(3)	0.0642(5)	1/4	0.6343(5)	3.5(2)
C(4)	0.1667(5)	1/4	0.6349(5)	3.8(2)
C(5)	0.2166(6)	1/4	0.5678(5)	4.2(2)
C(6)	0.1684(5)	1/4	0.4952(5)	3.8(2)
C(7)	0.2184(7)	1/4	0.4265(5)	4.8(3)
C(8)	0.0132(5)	1/4	0.7017(4)	3.6(2)
C(9)	0.1738(6)	1/4	0.3514(5)	5.4(3)
N(10)	0.1416(7)	1/4	0.2914(5)	7.8(3)
C(11)	0.3215(7)	1/4	0.4242(5)	5.5(3)
N(12)	0.4027(6)	1/4	0.4229(5)	7.5(3)
C(13)	-0.0896(6)	1/4	0.7049(5)	4.3(2)
N(14)	-0.1693(5)	1/4	0.7109(4)	5.7(2)
C(15)	0.0570(5)	1/4	0.7767(5)	4.1(2)
N(16)	0.0881(5)	1/4	0.8369(4)	5.8(3)
H(1)	0.016(6)	1/4	0.445(5)	7.0
H(2)	-0.056(6)	1/4	0.562(4)	7.0
H(4)	0.201(6)	1/4	0.683(5)	7.0
H(5)	0.289(6)	1/4	0.574(5)	7.0
(c) CH_3CN (on the mirror plane at y = 1/4)				
C(1')*	0.1437(7)	1/4	0.0865(7)	6.9(4)
C(2')	0.2442(8)	1/4	0.0683(6)	6.2(3)
N(3')	0.3231(7)	1/4	0.0544(6)	8.8(4)

* The methyl-carbon atom.

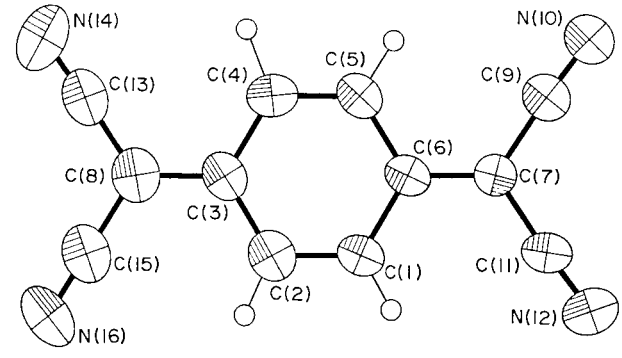

Figure 2. Molecular structure of TCNQ in the complex 3. Refer also to the legend of Figure 1. The molecules lie on the crystallographic mirror planes at y = 1/4 and 3/4.

Table 3

Selected Bond Distances with e.s.d.'s in Parentheses

atom - atom	distance/Å	atom - atom	distance/Å
(a) Tetramethoxydibenzo[*b*,*i*]thianthrene, **2**			
S(A) - C(1A)	1.751(5)	C(3A) - C(4A)	1.423(7)
S(B) - C(10A)	1.758(5)	C(3A) - C(8A)	1.429(7)
O(1A) - C(2A)	1.390(6)	C(4A) - C(5A)	1.378(8)
O(1A) - C(11A)	1.442(7)	C(5A) - C(6A)	1.400(9)
O(2A) - C(9A)	1.393(6)	C(6A) - C(7A)	1.391(8)
O(2A) - C(12A)	1.459(8)	C(7A) - C(8A)	1.414(7)
C(1A) - C(2A)	1.377(7)	C(8A) - C(9A)	1.411(7)
C(1A) - C(10A)	1.425(7)	C(9A) - C(10A)	1.378(7)
C(2A) - C(3A)	1.414(7)		
(b) TCNQ			
C(1) - C(2)	1.333(11)	C(7) - C(9)	1.446(13)
C(1) - C(6)	1.456(11)	C(7) - C(11)	1.447(13)
C(2) - C(3)	1.446(11)	C(8) - C(13)	1.444(11)
C(3) - C(4)	1.437(10)	C(8) - C(15)	1.439(11)
C(3) - C(8)	1.371(11)	C(9) - N(10)	1.134(12)
C(4) - C(5)	1.359(12)	C(11) - N(12)	1.139(12)
C(5) - C(6)	1.430(12)	C(13) - N(14)	1.122(11)
C(6) - C(7)	1.382(12)	C(15) - N(16)	1.131(11)
(c) CH_3CN			
C(1') - C(2')	1.444(15)	C(2') - N(3')	1.133(15)

Table 4

Selected Bond Angles with e.s.d.'s in Parentheses

atom - atom - atom	angle	atom - atom - atom	angle
(a) Tetramethoxydibenzo[*b*,*i*]thianthrene, **2**			
C(1A) - S(A) - C(10B)	106.4(2)	C(4A) - C(5A) - C(6A)	121.4(5)
C(2A) - O(1A) - C(11A)	111.9(4)	C(5A) - (C6A) - C(7A)	121.0(5)
C(9A) - O(2A) - C(12A)	112.2(4)	C(6A) - C(7A) - C(8A)	119.2(5)
S(A) - C(1A) - C(2A)	114.3(3)	C(3A) - C(8A) - C(7A)	119.5(4)
S(A) - C(1A) - C(10A)	127.1(3)	C(3A) - C(8A) - C(9A)	118.0(4)
C(2A) - C(1A) - C(10A)	118.6(4)	C(7A) - C(8A) - C(9A)	122.4(4)
O(1A) - C(2A) - C(1A)	117.8(4)	O(2A) - C(9A) - C(8A)	118.5(4)
O(1A) - C(2A) - C(3A)	119.0(4)	O(2A) - C(9A) - C(10A)	118.5(4)
C(1A) - C(2A) - C(3A)	123.1(4)	C(8A) - C(9A) - C(10A)	122.8(4)
C(2A) - C(3A) - C(4A)	122.2(5)	S(B) - C(10A) - C(1A)	126.5(4)
C(2A) - C(3A) - C(8A)	118.0(4)	S(B) - C(10A) - C(9A)	114.3(4)
C(4A) - C(3A) - C(8A)	119.7(5)	C(1A) - C(10A) - C(9A)	119.2(4)
C(3A) - C(4A) - C(5A)	119.1(5)		
(b) TCNQ			
C(2) - C(1) - C(6)	120.3(7)	C(6) - C(7) - C(9)	123.9(8)
C(1) - C(2) - C(3)	121.4(7)	C(6) - C(7) - C(11)	122.0(8)
C(2) - C(3) - C(4)	118.2(7)	C(9) - C(7) - C(11)	114.1(8)
C(2) - C(3) - C(8)	120.8(7)	C(3) - C(8) - C(13)	123.6(7)
C(4) - C(3) - C(8)	121.0(7)	C(3) - C(8) - C(15)	123.3(7)
C(3) - C(4) - C(5)	120.6(7)	C(13) - C(8) - C(15)	113.0(7)
C(4) - C(5) - C(6)	120.7(7)	C(7) - C(9) - N(10)	177.8(10)
C(1) - C(6) - C(5)	118.7(7)	C(7) - C(11) - N(12)	179.6(10)
C(1) - C(6) - C(7)	120.0(7)	C(8) - C(13) - N(14)	176.9(9)
C(5) - C(6) - C(7)	121.3(7)	C(8) - C(15) - N(16)	177.4(8)
(c) CH_3CN			
C(1') - C(2') - N(3')	179.7(11)		

what skewed but nearly planar over the five ring-system, but the methyl groups protrude oppositely from the molecular plane. On the other hand, the TCNQ and acetonitrile moieties lie on the crystallographic mirror plane at y = 1/4 and also at 3/4. The selected bond distances and angles are given in Tables 3 and 4, respectively. All these values are normal as compared with the reported values.

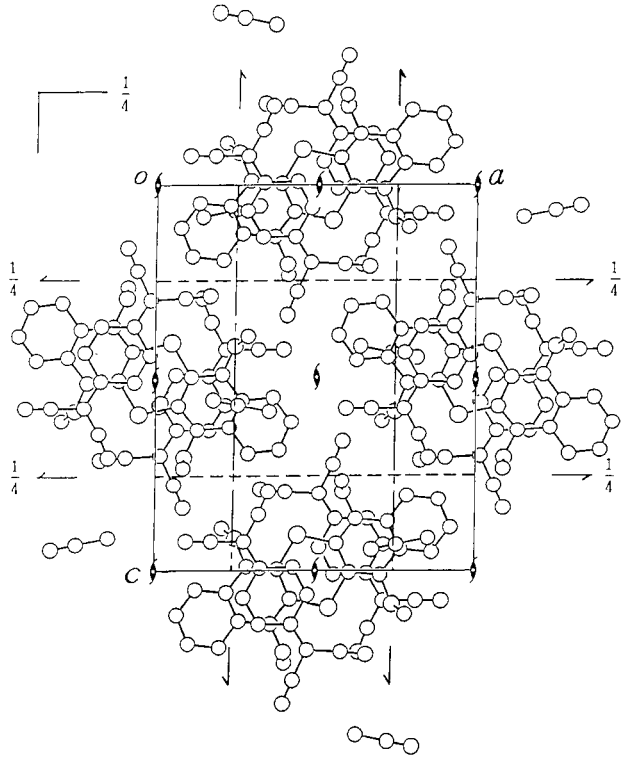

Figure 3. Crystal structure viewed along the b-axis.

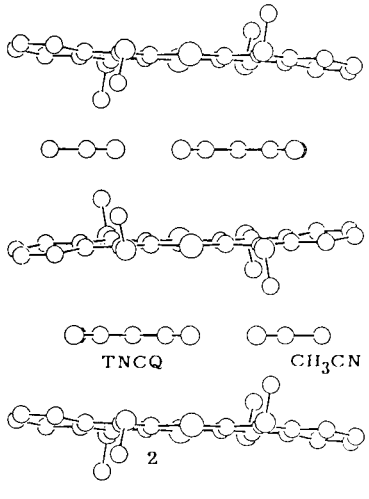

Figure 4. Mixed column consists of **2**, TCNQ, and CH_3CN, viewed along the long molecular axis of TCNQ.

The molecular packing of **3**, illustrated in Figures 3 and 4, shows that molecules **2** and TNCQ stack alternately along the b-axis to form a mixed stack. The solvent of crystallization, acetonitrile moiety, is located on the same plane with TCNQ to fill the vacant space in the crystals. The long molecular axes of **2** and TCNQ are almost perpendicular to each other. Since the methyl groups of **2** are out of the molecular plane, the intermolecular separation between the planes of **2** and TCNQ is about 3.4 Å, which is somewhat longer than the usual interplanar distance in conducting CT complexes. The conductivity of complex **3** is as low as an insulator as usually expected for those having a mixed stack, and moreover only very weak π-π interaction is probable owing to the loose steric arrangement of the methyl groups and the acetonitrile molecules. The mixed stacks assemble together to form a close packed structure.

In conclusion, the structure of **2** was directly confirmed by the present X-ray analysis, and consequently the structure of **1** was also established as reported previously [1].

REFERENCES AND NOTES

[1] M. Matsuoka, A. Iwamoto and T. Kitao, *J. Heterocyclic Chem.*, **28**, 1445 (1991).

[2] M. Matsuoka, A. Iwamoto, N. Furukawa and T. Kitao, *J. Heterocyclic Chem.*, **29**, 439 (1992).

[3] A. R. Katritzky and W.-Q. Fan, *J. Heterocyclic Chem.*, **25**, 901 (1988).

[4] A. R. Katritzky, W.-Q. Fan, Q.-L. Li and S. Bayyuk, *J. Heterocyclic Chem.*, **26**, 885 (1989).

[5] Preparations of single crystals of **1** and **2** were unsuccessful.

[6] The ^{1}H-nmr chemical shift of **3** in deuteriochloroform, compound **2**, 8.08, 8.07, 8.05, 8.04, (dd, 4H, J = 3.1), 7.53, 7.52, 7.50, 7.50 (dd, 4H, J = 3.1), 4.08 (s, 3H, OMe); TCNQ, 7.55 (s, 4H); CH_3CN, 2.01 (s, 3H).

[7] P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 78, Universities in York, England and in Louvain, Belgium, 1978.