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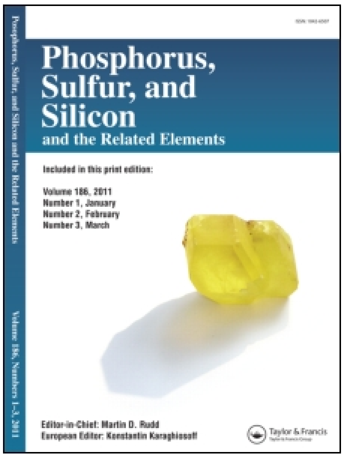

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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THE CRYSTAL STRUCTURES OF 9,10-DICHALCOGENAANTHRACENES, $C_{12}H_8XY$, (X, Y) = (S, Se), (S, Te), (Se, Te), and (O, Se)

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To cite this Article Meyers, E. A. , Irgolic, K. J. , Zingaro, R. A. , Junk, T. , Chakravorty, R. , Dereu, N. L. M. , French, K. and Pappalardo, G. C.(1988) 'THE CRYSTAL STRUCTURES OF 9,10-DICHALCOGENAANTHRACENES, $C_{12}H_8XY$, (X, Y) = (S, Se), (S, Te), (Se, Te), and (O, Se)', Phosphorus, Sulfur, and Silicon and the Related Elements, 38: 3, 257 — 269
To link to this Article: DOI: 10.1080/03086648808079721
URL: http://dx.doi.org/10.1080/03086648808079721

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Phosphorus and Sulfur, 1988, Vol. 38, pp. 257–269
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Abstract $C_{12}H_8SSe$ and $C_{12}H_8STe$ are monoclinic, $P2_1/c$, Z = 4/cell, isomorphous with $C_{12}H_8S_2$ and $C_{12}H_8Se_2$. $C_{12}H_8SSe$ and $C_{12}H_8STe$ are both disordered with unequal occupancies of the two chalcogen sites. Similarly, $C_{12}H_8SeTe$ is disordered, orthorhombic Pbca, Z = 8/cell, isomorphous with $C_{12}H_8Te_2$ and has unequal occupancies of its chalcogen sites. Because of the disorder, only average values of the molecular dimensions could be found. Within this limitation, bond angles and bond distances appear to be normal, as do the angles of fold in these butterfly-shaped molecules. The crystals of of $C_{12}H_8OSe$ were of poor quality, frequently twinned. The structure determined from the x-ray data is isomorphous with those of $C_{12}H_8OS$ and $C_{12}H_8OTe$. The crystals are orthorhombic $P2_12_12_1$.

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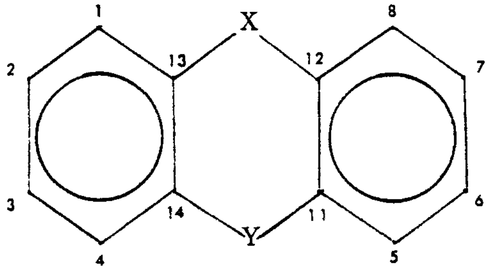
INTRODUCTION

The systematic study of structural regularities of related compounds is a desirable goal, but one which is often hampered by missing information. In order to allow comparisons to be made among 9,10-dichalcogenaanthracenes, $C_{12}H_8XY$, (I),



(I)

with X,Y representing any of the common chalcogens, O, S, Se or Te, x-ray crystal structure determinations were carried out for the compounds with (X,Y) = (S,Se), (S,Te), (Se,Te) and (O,Se). The results have proved to be less informative than had been hoped, because crystals of the first three compounds were disordered, and the best crystals obtained for (O,Se) were of marginal quality. Despite these problems, structural comparisons can be made now for all of these compounds.

DETERMINATION OF CRYSTAL STRUCTURES

X-ray data were collected by the Molecular Structure Corporation, College Station, Texas. Details regarding the data collection and the results of refinement are given in TABLE I and final coordinates and equivalent isotropic temperature factors are given in TABLE II. Finding trial structures was extremely simple since it was apparent from the unit cell dimensions that each of these compounds is isomorphous with at least one other 9,10-dichalcogenaanthracene of previously determined structure: $C_{12}H_8OSe$ is isomorphous with $C_{12}H_8OS$[1] and with $C_{12}H_8OTe$[2] ; $C_{12}H_8SSe$ and $C_{12}H_8STe$ are isomorphous with $C_{12}H_8S_2$[3] and $C_{12}H_8Se_2$[4] ; $C_{12}H_8SeTe$ is isomorphous with $C_{12}H_8Te_2$[5]. The trial structure for $C_{12}H_8OSe$ refined satisfactorily, but it was obvious immediately upon inspection of electron density maps that the chalcogen positions were disordered in the other three compounds. In order to approximate the scattering from the atoms at the sites labeled "X1" and "X2", the scattering factor of Se was used for (S,Se) and (S,Te) and that of Te for (Se,Te). The occupancies "K1" and "K2" were then allowed to vary in least squares refinements as well as coordinates and anisotropic temperature factors. H-atoms were added to the structures and fixed in position with (C-H) = 1.08 Å for (S,Se) and (S,Te) and (C-H) = 0.96 Å for the others. Weighted least-squares refinements on the structure factors were carried out for the carbon and chalcogen atom variables until the shifts in all parameters became less

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TABLE I Summary of X-ray information for C12 H8 X Y.

X	O	Se	S	S	Se
Y	Se	Se	Se	Te	Te
Mr	247.1	310.1	263.2	311.9	358.7
λ(A)	0.71073	0.71073	0.71073	0.71073	0.71073
T(K)	296	296	296	296	183
Crystal size (mm)	0.30 0.15 0.15	0.15 0.15 0.10	0.35 0.20 0.15	0.30 0.18 0.10	0.35 0.25 0.05
a(A)	5.941(1)	12.128(2)	12.019(2)	12.286(4)	6.464(1)
b(A)	7.926(2)	6.262(1)	6.221(1)	6.446(2)	15.005(3)
c(A)	20.727(4)	14.624(3)	14.522(2)	14.580(4)	22.479(5)
α(deg)	90	90	90	90	90
β(deg)	90	109.94(1)	109.82(1)	111.04(2)	90
γ(deg)	90	90	90	90	90
V(A**3)	976.1(4)	1044.0(3)	1021.5(3)	1084.7(6)	2180.3(7)
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbca
Z	4	4	4	4	8
F(000)	488	592	520	592	1328
Dx(gmcm**-3)	1.68	1.97	1.71	1.91	2.19
μ(cm**-1)	37.6	69.7	37.9	28.9	60.0
Emp. abs. corr.	0.84 < t t < 1.00	None	0.66 < t t < 1.00	0.88 < t t < 1.00	0.53 < t t < 1.00
2θ,max (deg)	50	50	60	52	60
No. ref.	1205	1457	1747	1508	2665
Fobs/sigma	> 3.0	> 1.0	> 1.0	> 1.0	> 5.0
R	0.075	0.044	0.061	0.060	0.066
Std. error	1.54	1.38	1.33	1.63	1.56
Diff. el. density (e/A**3)	-0.94 < e e < 1.10	-1.07 < e e < 0.85	-0.44 < e e < 0.56	-0.74 < e e < 0.70	-1.17 < e e < 1.72
Misc. info.	ω-scan Rigaku AFC6R	ω/2θ-scan Nonius CAD4	ω/2θ-scan Nonius CAD4	ω/2θ-scan Nonius CAD4	ω/2θ-scan Nonius CAD4

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TABLE II Coordinates and equivalent isotropic temperature factors for C12 H8 X Y.

(1) X - O, Y - Se

ATOM	x/a	y/b	z/c	Ueq
O	0.3902(12)	0.3311(11)	0.3643(4)	0.0535(31)
Se	-0.0569(2)	0.1251(2)	0.3627(1)	0.0567(4)
C1	0.2928(25)	0.5213(18)	0.4480(6)	0.0521(53)
C2	0.1538(28)	0.5730(18)	0.4964(6)	0.0547(55)
C3	-0.0546(30)	0.4953(19)	0.5035(6)	0.0568(54)
C4	-0.1216(19)	0.3687(20)	0.4623(5)	0.0494(49)
C5	0.0680(26)	0.1530(17)	0.2285(6)	0.0584(53)
C6	0.2060(28)	0.1944(18)	0.1771(6)	0.0600(58)
C7	0.4022(24)	0.2805(17)	0.1905(6)	0.0571(57)
C8	0.4622(23)	0.3259(14)	0.2518(6)	0.0452(47)
C11	0.1251(22)	0.1976(15)	0.2920(6)	0.0450(50)
C12	0.3216(24)	0.2834(17)	0.3022(6)	0.0450(49)
C13	0.2323(19)	0.3851(17)	0.4079(5)	0.0369(40)
C14	0.0206(20)	0.3117(15)	0.4143(5)	0.0405(44)

(2) X - Se, Y - Se

ATOM	x/a	y/b	z/c	Ueq
Se1	0.35471(6)	-0.07574(10)	0.03721(5)	0.0427(3)
Se2	0.23474(6)	0.38001(10)	0.07888(5)	0.0483(3)
C1	0.1292(6)	-0.1452(11)	-0.1059(5)	0.0484(27)
C2	0.0147(6)	-0.0961(12)	-0.1600(5)	0.0549(29)
C3	0.0346(6)	0.0916(13)	-0.1436(5)	0.0544(28)
C4	0.0304(6)	0.2300(11)	-0.0725(4)	0.0471(26)
C5	0.3058(6)	0.2294(11)	0.2747(5)	0.0499(26)
C6	0.3611(6)	0.0884(13)	0.3512(5)	0.0586(30)
C7	0.4077(6)	-0.0959(12)	0.3326(5)	0.0562(28)
C8	0.4021(5)	-0.1516(10)	0.2388(5)	0.0452(25)
C11	0.3027(5)	0.1812(10)	0.1808(4)	0.0381(22)
C12	0.3516(5)	-0.0081(10)	0.1631(4)	0.0371(22)
C13	0.1965(5)	-0.0068(10)	-0.0348(4)	0.0384(22)
C14	0.1457(5)	0.1838(10)	-0.0180(4)	0.0413(24)

(3) X - S, Y - Se; K1 - 0.626(3), K2 - 0.742(3)

ATOM	x/a	y/b	z/c	Ueq
X1	0.35400(7)	-0.07813(12)	0.04097(6)	0.0502(3)
X2	0.23471(6)	0.38108(9)	0.08155(5)	0.0526(3)
C1	0.1328(4)	-0.1500(7)	-0.1013(3)	0.0531(20)
C2	0.0181(4)	-0.0994(8)	-0.1586(3)	0.0604(21)
C3	-0.0313(4)	0.0922(9)	-0.1434(3)	0.0576(20)
C4	0.0333(4)	0.2332(7)	-0.0715(3)	0.0503(18)
C5	0.3056(4)	0.2309(8)	0.2757(3)	0.0563(20)
C6	0.3610(4)	0.0917(9)	0.3520(3)	0.0632(22)
C7	0.4076(4)	-0.0979(8)	0.3347(4)	0.0618(21)
C8	0.4006(4)	-0.1524(7)	0.2395(4)	0.0506(18)
C11	0.3009(3)	0.1843(7)	0.1808(3)	0.0429(16)
C12	0.3498(3)	-0.0100(7)	0.1632(3)	0.0401(16)
C13	0.1995(4)	-0.0085(7)	-0.0296(3)	0.0423(17)
C14	0.1490(4)	0.1844(7)	-0.0147(3)	0.0454(17)

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TABLE II Coordinates and equivalent isotropic temperature factors for C12 H8 X Y. (Continued.)

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(4) X = S, Y = Te; K1 = 0.744(4), K2 = 1.117(6)

ATOM	x/a	y/b	z/c	Ueq
X1	0.36057(11)	-0.07272(18)	0.03987(9)	0.0840(6)
X2	0.23397(6)	0.39658(10)	0.08653(5)	0.0713(3)
C1	0.1352(7)	-0.1418(12)	-0.1006(6)	0.0775(37)
C2	0.0211(8)	-0.1038(16)	-0.1579(6)	0.0871(41)
C3	-0.0302(7)	0.0792(16)	-0.1448(6)	0.0792(36)
C4	0.0303(6)	0.2192(12)	-0.0739(6)	0.0735(34)
C5	0.3108(7)	0.2134(14)	0.2852(7)	0.0843(40)
C6	0.3659(8)	0.0689(20)	0.3557(6)	0.1056(49)
C7	0.4100(8)	-0.1124(17)	0.3320(8)	0.1057(48)
C8	0.4014(6)	-0.1493(14)	0.2393(7)	0.0804(37)
C11	0.3041(6)	0.1766(11)	0.1887(5)	0.0606(28)
C12	0.3506(5)	-0.0055(10)	0.1662(5)	0.0552(27)
C13	0.1990(6)	-0.0038(11)	-0.0299(5)	0.0611(29)
C14	0.1451(6)	0.1800(11)	-0.0168(5)	0.0610(29)

(5) X = Se, Y = Te; K1 = 0.774(5), K2 = 0.816(5)

ATOM	x/a	y/b	z/c	Ueq
X1	-0.38996(12)	-0.02168(6)	0.11980(4)	0.0461(3)
X2	0.06512(11)	0.05244(5)	0.18742(3)	0.0420(3)
C1	-0.2309(16)	0.0811(7)	0.0169(4)	0.0470(34)
C2	-0.0978(18)	0.1344(6)	-0.0142(4)	0.0553(39)
C3	0.0870(17)	0.1626(7)	0.0123(5)	0.0545(38)
C4	0.1335(15)	0.1371(6)	0.0694(4)	0.0477(35)
C5	0.1420(16)	-0.1418(7)	0.1998(4)	0.0517(38)
C6	0.0931(22)	-0.2315(8)	0.1972(5)	0.0716(50)
C7	-0.0890(25)	-0.2594(7)	0.1708(5)	0.0720(50)
C8	-0.2242(17)	-0.1982(7)	0.1458(4)	0.0542(37)
C11	-0.0008(13)	-0.0787(6)	0.1778(4)	0.0361(29)
C12	-0.1828(14)	-0.1084(6)	0.1503(4)	0.0426(32)
C13	-0.1871(13)	0.0558(6)	0.0746(4)	0.0379(29)
C14	-0.0025(13)	0.0842(6)	0.1020(4)	0.0357(29)

K1 and K2 represent relative occupancies of the sites X1 and X2, respectively, and are discussed in the text.

$U_{eq}/(A^2) = 1/3 \sum U(i,j)a(i)^* a(j)^* \hat{a}(i) \cdot \hat{a}(j)$

than 0.1 of their corresponding standard deviations. The weights were estimated from $\sigma^2(I) = s^2(I) + 0.05I$, where $s^2(I)$ was obtained from counting statistics. The program used for the calculations was SHELX76[6]. (In addition to the new x-ray work reported here, similar information for (Se,Se) is included in TABLE I and TABLE II. The original report of the structure[4] did not include these details.) After these calculations were completed, a number of changes in the refinement procedures were tested in order to determine their influence on the final results. Because of the non-linear form of the analytical representation of the scattering factors[7], it is difficult to introduce good approximations for the scattering from disordered structures such as those encountered here. A procedure designed to overcome this problem has been reported recently[8], but a simpler and less accurate method was applied to $C_{12}H_8STe$. The scattering factors[7] for S and Te were fitted by least-squares to five term expressions of the following form

$$f^* = a * exp[-0.2u] + b * exp[-1.0u] + c * exp[-10.0u] + d * exp[-40.0u] + e$$

where $u = (\sin\theta/\lambda)^2$, $0 \leq u \leq 0.49$. It was assumed that the relative number of electrons at sites "X1" and "X2" were in the ratio K1/K2, and that their sum was 68 (S with 16 electrons, Te with 52 electrons). From this, site "X1" is estimated to possess 27.2 electrons. Assuming that S supplies 16 electrons per atom and that Te supplies 52 electrons per atom, the fractional occupancies of site "X1" are S(0.689) and Te(0.311). The average scattering factor for site "X1" was calculated as 0.689 $f^*(S)$ + 0.311 $f^*(Te)$, and for "X2" as 0.311 $f^*(S)$ + 0.689 $f^*(Te)$. Least-squares refinement of occupancies, coordinates and anisotropic temperature factors was carried out as described previously. The R-factor improved slightly, from 0.0601 to 0.0593, the occupancy factors became K1 = 0.972(5), K2 = 0.955(5) and all bond distances and bond angles differed by less than 0.6σ from the original values. Next, the effect of changing (C-H) from 1.08 Å to 0.96 Å was tested. The R-factor improved slightly again, to R = 0.0588, the occupancies became K1 = 0.983(5),

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K2 = 0.966(5), and all bond distances and bond angles differed by less than 0.8σ from the original values. The original values have been retained in the tables.

In order to examine the behavior of the occupancy factors for an ordered structure, the data for (Se,Se) were refined with variable occupancies. Values of K1 = 0.979(4) and K2 = 0.980(5) were obtained and the value of R = 0.0442 was unchanged. Thus, it seems that the values of K1 and K2 obtained for (S,Te) are not unreasonable.

DISCUSSION

Bond distances, bond angles and interplanar angles are given in TABLE III, TABLE IV AND TABLE V. The structure of anthracene, $C_{12}H_{10}$, has been determined very carefully, and the variation in its (C-C) distances analyzed in great detail[9,10]. Using the same numbering system as in (I), the shortest (C-C) distance in perdeuteroanthracene[11] is (1,2) = 1.368(2)Å and the longest is (1,13) = 1.439(3)Å. This range in (C-C) distances is larger than any found for $C_{12}H_8XY$, including those molecules not presented in the tables, (O,O)[12], (O,S)[1], (O,Te)[2], (S,S)[3] and (Te,Te)[5]. Since in the case of anthracene, simple Hückel π - electron calculations give reasonably good correlations of bond distance with Coulson bond order, similar calculations were performed for the molecules $C_{12}H_8XY$[13]. First, 16 electrons (rather than 14) were placed in the π- system and the parameters "h" and "k" (described in references 13 and 14) were varied: $0.33 \leq h \leq 2.0$, $0.20 \leq k \leq 1.0$, with S = 0. The introduction of two extra electrons produced several obvious changes: the range of bond orders was diminished from (0.7314,0.4849) to (0.6826,0.5014), and the largest bond order was associated with bond (2,3) and the smallest with (11,12). Similar results, with even smaller variations in bond order were obtained in the other calculations. The decrease in range agrees well with experiment, and for all ten possible structures, the weighted mean bond distances

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TABLE III (C - C) Bond distances (A) and internal angles of the C-atom rings, (C - C - C) (deg), of C12 H8 X Y

(X, Y)	(O,Se)	(S,Se)	(S,Te)	(Se,Se)	(Se,Te)
(1 - 13)	1.410(23)	1.391(6)	1.384(10)	1.385(7)	1.382(15)
(8 - 12)	1.380(23)	1.387(6)	1.389(10)	1.394(6)	1.377(16)
(4 - 14)	1.381(20)	1.388(6)	1.394(10)	1.383(7)	1.393(15)
(5 - 11)	1.404(21)	1.391(6)	1.401(10)	1.394(6)	1.412(16)
(1 - 2)	1.362(23)	1.385(6)	1.386(12)	1.378(8)	1.367(16)
(7 - 8)	1.367(21)	1.398(6)	1.339(13)	1.394(7)	1.386(19)
(3 - 4)	1.376(24)	1.383(6)	1.382(11)	1.376(7)	1.373(17)
(5 - 6)	1.384(24)	1.385(7)	1.381(13)	1.403(7)	1.383(19)
(2 - 3)	1.391(26)	1.382(7)	1.381(12)	1.376(8)	1.401(17)
(6 - 7)	1.379(26)	1.365(7)	1.381(14)	1.353(8)	1.383(20)
(13 - 14)	1.392(21)	1.395(6)	1.402(10)	1.403(7)	1.409(14)
(11 - 12)	1.368(23)	1.405(6)	1.393(10)	1.389(7)	1.402(15)
(2 - 1 - 13)	120.7(18)	120.6(4)	122.2(8)	120.8(5)	120.9(11)
(7 - 8 - 12)	118.8(18)	119.8(4)	121.0(9)	118.8(5)	119.7(13)
(3 - 4 - 14)	120.6(17)	120.2(4)	120.2(7)	120.7(5)	120.9(11)
(6 - 5 - 11)	121.3(19)	120.6(4)	118.6(8)	119.6(5)	119.2(13)
(1 - 2 - 3)	119.0(18)	119.6(4)	118.9(8)	120.2(5)	119.7(12)
(6 - 7 - 8)	122.6(18)	120.0(4)	120.1(9)	121.8(5)	120.6(13)
(2 - 3 - 4)	121.0(18)	120.4(4)	120.5(8)	119.9(5)	120.0(11)
(5 - 6 - 7)	117.5(18)	120.6(4)	121.2(8)	119.8(5)	120.5(14)
(8 - 12 - 11)	121.4(16)	120.2(4)	119.7(7)	120.1(4)	120.4(12)
(1 - 13 - 14)	119.6(16)	119.4(4)	118.1(7)	118.8(5)	120.0(10)
(5 - 11 - 12)	118.5(18)	118.7(4)	119.4(7)	119.9(4)	119.4(11)
(4 - 14 - 13)	119.5(16)	119.8(4)	120.1(7)	119.6(4)	118.5(10)

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TABLE IV Bond distances (Å) and internal angles (deg) of central ring for C12 H8 X Y

(X, Y)	(O,Se)	(S,Se)	(S,Te)	(Se,Se)	(Se,Te)
(X - 12)	1.402(18)	1.843(4)	1.937(7)	1.902(4)	1.989(12)
(X - 13)	1.370(17)	1.843(4)	1.946(7)	1.897(5)	2.025(11)
(Y - 11)	1.910(17)	1.852(4)	2.023(7)	1.901(5)	2.025(11)
(Y - 14)	1.882(16)	1.880(4)	2.070(7)	1.908(5)	2.026(11)
(13 - 14)	1.392(21)	1.395(5)	1.402(10)	1.403(7)	1.409(14)
(11 - 12)	1.368(23)	1.405(6)	1.393(10)	1.389(7)	1.402(15)
(12 - X - 13)	119.4(12)	97.5(2)	93.5(3)	97.8(2)	96.4(4)
(11 - Y - 14)	93.5(7)	97.5(2)	92.8(3)	98.3(2)	94.7(4)
(X - 12 - 11)	121.6(16)	121.5(3)	125.2(5)	121.4(3)	120.6(9)
(X - 13 - 14)	123.4(16)	121.7(3)	124.5(6)	121.2(3)	120.2(8)
(Y - 11 - 12)	120.9(13)	121.5(3)	121.6(5)	120.8(3)	122.2(9)
(Y - 14 - 13)	119.7(12)	121.3(3)	120.9(5)	120.4(4)	121.7(8)

In these disordered structures, the labels "X" and "Y" refer to the sites "X1" and "X2" as discussed in the text.

TABLE V Angles (deg) between best planes of C12 H8 X Y

Plane I : (X,Y,C13,C14) Plane II : (X,Y,C11,C12)
Plane III : (C1,C2,C3,C4,C13,C14) Plane IV : (C5,C6,C7,C8,C11,C12)

(X, Y)	(O,Se)	(S,Se)	(S,Te)	(Se,Se)	(Se,Te)
(I) - (II)	139.7	123.7	120.2	123.4	119.9
(III) - (IV)	147.0	128.3	126.8	126.8	122.8

In these disordered structures, the labels "X" and "Y" refer to the sites "X1" and "X2" as discussed in the text.

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are (2,3) = (6,7) = 1.374(2)Å; (11,12) = (13,14) = 1.393(3)Å; (1,13) = (8,12) = 1.388(1)Å; (4,14) = (5,11) = 1.389(2)Å; (1,2) = (7,8) = 1.392(3)Å; (3,4) = (5,6) = 1.392(2)Å. These values were not corrected for thermal motion.

The interior angles of the benzene-like rings of $C_{12}H_8XY$ vary over a relatively narrow range. Correlations have been found between interior phenyl ring angles and substituent characteristics, especially electronegativities[15]. It was reported previously that qualitative agreement with these correlations was found for $C_{12}H_8XY$[4]. The narrow range of angles and the disorder in the structures reported here prevent the making of quantitative statements.

The mean bond distances, (C-O) = 1.386 Å and (C-Se) = 1.896 Å in $C_{12}H_8OSe$ are normal. The bond angles at O and at Se fall into the patterns exhibited previously: for $C_{12}H_8OY$, the angles with apex at O are (116.3°, 118°,119.4°,121.4°) for Y = (O,S,Se,Te) while the corresponding angles at apex Y are (116.3°,97°, 93.5°,89.4°). In comparison, for (Y,Y), the (average) angles at Y are (116.3°, 100°,98.0°,95.6°) for Y = (O,S,Se,Te). Thus, the angle at O increases steadily in the series cited for $C_{12}H_8OY$, while the angles at Y ($Y \neq O$) are systematically smaller than the corresponding values for $C_{12}H_8Y_2$. A simple model can account for these trends. If the C-atom rings are assumed to be regular hexagons with bond angles of 120° and that the (C-Y) bond distances and (C-Y-C) bond angles of $C_{12}H_8Y_2$ are "normal" values, then the variation of the angles at X and Y in $C_{12}H_8XY$ can be calculated as the central ring is folded, keeping the bond distances fixed.

$$[1.39 + (C - X)] * sin[(C - X - C)/2] = [1.39 + (C - Y)] * sin[(C - Y - C)/2]$$

For example, in (O,O), (C-O) = 1.382 Å, (C-O-C) = 116.3°; in (Se,Se), (C-Se) = 1.902 Å, (C-Se-C) = 98.0°. Then, if (C-O-C) = 116.3° in $C_{12}H_8OSe$, the angle (C-Se-C) is calculated to be 91.3°, while if (C-Se-C) were 98.0°, (C-O-C) would be 127.4°. In the actual structure a compromise is reached between these extremes:

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(C-O-C) = 119.4° and (C-Se-C) = 93.5°. Similar estimates can be made for the other molecules (O,Y) and similar results are obtained.

Because (S,Se), (S,Te) and (Se,Te) have disordered structures, it is difficult to compare their carbon-chalcogen bond distances with those obtained from the ordered structures. It was assumed that these distances in $C_{12}H_8XY$ should be compared to ones calculated as averages, weighted by the appropriate atomic number, Z, and by the appropriate mole fraction, f, at the given site:

$$\frac{Z_x * f_x * (C - X) + Z_y * f_y * (C - Y)}{Z_x * f_x + Z_y * f_y}$$

with (C-X) and (C-Y) taken as the average distances obtained from the ordered structures $C_{12}H_8X_2$ and $C_{12}H_8Y_2$ respectively. To illustrate, for (S,Te), (C-S) = 1.762Å, (C-Te) = 2.112Å; $Z_s = 16$, $Z_{te} = 52$; f = 0.311 or 0.689: calculated (C-X1) = 1.970Å, (C-X2) = 2.069Å, compared to (1.942Å, 2.042Å) obtained experimentally. The values calculated without weighting by Z are much worse, namely 1.871Å and 2.003Å. Using the value (C-Se) = 1.902Å, the calculated weighted distances for (S,Se) are (1.842Å, 1.870Å) compared to experiment, (1.843Å, 1.866Å) and for (Se,Te) are (2.016Å, 2.041Å) compared to the measured values (2.007Å, 2.026Å). The angles (C-X-C) in the ordered 9,10-dichalcogenaanthracenes decrease in the sequence X = O > S > Se > Te. The same trend is seen in the disordered structures and, moreover, (C-X1-C) ≤ (C-X2-C) in each individual case.

The interplanar angles are listed in TABLE V. In each case the angle of fold of the central ring, θ_2, is less than that between the benzene-like outer rings, θ_1, a result which is obtained for all $C_{12}H_8XY$ except (O,O). The variations in θ_1 and θ_2 are monotonic for $C_{12}H_8OY$: (O,O) = ($\sim 180°, \sim 180°$); (O,S) = ($150°, 141°$); (O,Se) = ($147°, 140°$); (O,Te) = ($145°, 138°$). The angular variations are almost as regular in the remaining structures, but only average values have been obtained for the disordered cases and the total variation in θ_1 and θ_2 is only from 130° to 120° for $C_{12}H_8XY$, with X,Y $\neq$O.

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In recent years, a number of structures, $C_{12}H_8XZ$, have been determined in which Z is a disubstituted Group IV element[16-24]. Their (C-O), (C-S) and (C-Te) bond distances agree well with those obtained from the structures of $C_{12}H_8XY$ and (C-O-C) > (C-S-C) > (C-Te-C). The molecules are folded, but there is a wide variation in the angles of fold. In a recent structure determination of 10,10'-*bis*(phenoxarsine oxide, $(C_{12}H_8OAs)_2O$, it was found that the two $C_{12}H_8OAs$ portions of the same molecule have widely different angles of fold, with θ_2 = 175°, 154°. This implies that these rings bend easily, a suggestion that had been made previously[26]. In contrast, for the molecules $C_{12}H_8XY$, more rigid conformations seem to be indicated from the available structural evidence.

Acknowledgements: Financial support of these investigations by the U.S. National Science Foundation, CNR of Italy (Progetto bilaterale US-Italia) and the Robert A. Welch Foundation of Houston, Texas is gratefully acknowledged.

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