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The Crystal and Molecular Structures of 9-Anthryl Styryl Ketone and 9,10-Anthryl Bis(Styryl Ketone)

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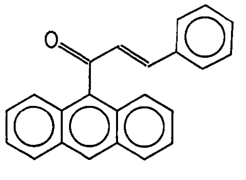
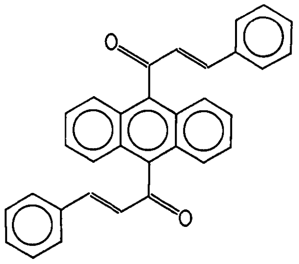
Investigation of the structures of 9-anthryl styryl ketone, $C_{14}H_9$–CO–CH=CH–C_6H_5 (ASK), and 9,10-anthryl bis(styryl ketone), $C_{14}H_8$–(CO–CH=CH–C_6H_5)$_2$ (ABSK), was prompted by studies of chemical reactions which demonstrated that ASK, under Friedel–Crafts conditions, disproportionated to anthracene and ABSK rather than rearranging to the 1- and 2-isomers as has been noted for 9-acetylanthracene. Crystals of both compounds are triclinic with space group $P\bar{1}$. Unit-cell parameters are: for ASK, $a=9{\cdot}448$ (1), $b=10{\cdot}369$ (1), $c=8{\cdot}590$ (1) Å, $\alpha=102{\cdot}14$ (1), $\beta=102{\cdot}45$ (1), $\gamma=91{\cdot}11$ (1)°, $Z=2$; for ABSK, $a=10{\cdot}878$ (1), $b=12{\cdot}407$ (1), $c=10{\cdot}803$ (1) Å, $\alpha=120{\cdot}23$ (1), $\beta=108{\cdot}82$ (1), $\gamma=87{\cdot}71$ (1)°, $Z=2$. Full-matrix least-squares refinement of all positional and thermal (anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms) parameters converged at conventional R's of 0·046 (ASK) and 0·052 (ABSK) using 2184 and 2439 reflections [$I>3\sigma(I)$], respectively. Intensities were measured on a Syntex diffractometer with Mo $K\alpha$ radiation. The two molecules are basically similar, the plane of the keto group being rotated about 78° from the plane of the anthracene ring. The atoms in each of the anthracene rings deviate only by small amounts from the best plane through their respective rings; the largest deviation is 0·021 Å. Bond distances and angles for the anthracene rings of the two molecules are compared with those of anthracene and several 9,10-substituted anthracenes.

Introduction

Under Friedel–Crafts conditions, some 9-acylanthracenes disproportionate to yield anthracene and the corresponding 9,10-diacylanthracenes while others simply rearrange to give the 1- and 2-isomers. 9-Anthryl styryl ketone, ASK, $C_{14}H_9$–CO–CH=CH–C_6H_5, disproportionates to form 9,10-anthryl bis(styryl ketone), ABSK, $C_{14}H_8$–(CO–CH=CH–C_6H_5)$_2$; 9-acetylanthracene is the most common example of a compound which undergoes 1- and 2-isomerization. (See Dlamini, Williams & Shotter (1973) for a complete discussion and references.)



ASK



ABSK

This anomalous behavior has led to the present study to examine differences in the structures of ASK and ABSK which might help to explain the chemical results. Differences to be particularly noted would include: steric effects between the acyl group and the hydrogen atoms at the 1- and 8-positions of the anthracene ring; π overlap between the anthracene ring and the styryl-keto group; and distortions in geometry of the anthracene ring.

Experimental

Yellow crystals of ASK were grown from xylene solutions by slow evaporation. ABSK crystals, also yellow in color, were grown by sublimation after it was discovered that solvent molecules were readily included in crystals grown from benzene, toluene, and other solvents. The two crystals selected for this study had the following dimensions: ASK, 0·26 × 0·35 × 0·39 × 0·50 mm perpendicular to (1$\bar{1}$0), (10$\bar{1}$), (010), and (100) respectively; ABSK, 0·25 × 0·36 × 0·39 × 0·47 mm perpendicular to (1$\bar{1}$0), (01$\bar{1}$), (100), and (010) respectively. Crystal data for the two compounds are listed in Table 1. Each set of unit-cell parameters is the result of a least-squares refinement of the Bragg angles of well resolved Cu $K\alpha_1$ peaks as measured on a G.E. XRD-5 diffractometer. For ASK, 27 reflections ($73° < 2\theta < 112°$), and for ABSK, 30 reflections ($90° < 2\theta < 113°$) were used in the refinement.

Table 1. *Crystal data for ASK and ABSK*

	ASK	ABSK*
Formula	$C_{23}H_{16}O$	$C_{32}H_{22}O_2$
M.W.	308·38	438·53
Crystal class	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9·448 (1)	10·878 (1)
b (Å)	10·369 (1)	12·407 (1)
c (Å)	8·590 (1)	10·803 (1)
α (°)	102·14 (1)	120·23 (1)
β (°)	102·45 (1)	108·82 (1)
γ (°)	91·11 (1)	87·71 (1)
d_m (g cm^{-3})	1·277	1·237
d_x (g cm^{-3})	1·277	1·235
Z	2	2
μ(Mo $K\alpha$) (cm^{-1})	0·83	0·80

* It was properly pointed out by one referee that the cell dimensions for ABSK do not conform to the Donnay convention; in accord with this convention, the cell dimensions would be $a = 10·878$ (1), $b = 11·649$ (1), $c = 10·803$ (1) Å, $\alpha = 113·03$ (1), $\beta = 108·82$ (1), and $\gamma = 75·13$ (1)°.

ASK data collection

Intensity data were collected on a Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite crystal. The θ–2θ scan technique was employed with each scan ranging from 0·8° in 2θ below the $K\alpha_1$ peak to 1·0° beyond the $K\alpha_2$ peak; P counts were accumulated. The scan rate, S, varied from 1·5 to 4·0° min^{-1} depending on the number of counts measured in a rapid preliminary scan. Background counts, B_1 and B_2, were taken at both ends of the scan range, each for a time equal to half the scan time. A total of 3707 unique reflections of the type $h, \pm k, \pm l$ were measured in the range $4° < 2\theta < 55°$. The intensities of four standard reflections were measured after every 96 reflections; only statistical variations were noted. Coincidence losses were corrected *via* direct knowledge of the counting system's dead time.

ABSK data collection

A total of 4113 reflections ($4° < 2\theta < 50°$) were measured on the Syntex diffractometer using ω scans instead of θ–2θ scans in order to shorten the data-collection period. Scans of 1·2° were used with the scan rate varying from 1·5 to 5·0° min^{-1}. Backgrounds were

Table 2. *Atomic coordinates and thermal parameters for ASK*

(a) Non-hydrogen atoms. Positional and thermal parameters are × 10^4. The thermal parameters are of the form $\exp[-(h^2\beta_{11} + \ldots + 2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	5162 (3)	3043 (3)	4845 (3)	114 (4)	96 (3)	168 (6)	10 (3)	43 (4)	35 (4)
C(2)	5667 (3)	3026 (3)	3477 (4)	136 (5)	132 (4)	245 (7)	21 (4)	73 (5)	91 (5)
C(3)	5289 (3)	1964 (3)	2103 (4)	155 (5)	169 (5)	165 (6)	52 (4)	72 (5)	66 (5)
C(4)	4417 (3)	935 (3)	2139 (3)	138 (4)	131 (4)	135 (6)	42 (4)	41 (4)	30 (4)
C(5)	1418 (3)	−1247 (3)	4976 (4)	127 (4)	77 (3)	182 (6)	−8 (3)	26 (4)	8 (4)
C(6)	903 (3)	−1278 (3)	6305 (4)	130 (4)	90 (4)	249 (7)	−19 (3)	47 (5)	33 (4)
C(7)	1299 (3)	−243 (3)	7716 (4)	133 (4)	112 (4)	190 (6)	7 (3)	68 (4)	42 (4)
C(8)	2191 (3)	796 (3)	7736 (3)	116 (4)	85 (3)	139 (5)	6 (3)	44 (4)	10 (3)
C(9)	3679 (2)	1950 (2)	6320 (3)	71 (3)	69 (3)	114 (4)	18 (2)	13 (3)	13 (3)
C(10)	2933 (3)	−142 (3)	3589 (3)	113 (4)	84 (3)	118 (5)	23 (3)	8 (4)	−8 (3)
C(11)	2366 (2)	−182 (2)	4941 (3)	86 (3)	73 (3)	127 (5)	10 (2)	12 (3)	17 (3)
C(12)	2752 (2)	885 (2)	6350 (3)	77 (3)	71 (3)	113 (4)	15 (2)	16 (3)	12 (3)
C(13)	4231 (2)	1978 (2)	4930 (3)	77 (3)	77 (3)	124 (5)	17 (2)	19 (3)	27 (3)
C(14)	3851 (2)	903 (2)	3539 (3)	96 (3)	92 (3)	109 (4)	29 (3)	25 (3)	26 (3)
C(15)	4178 (2)	3041 (2)	7823 (3)	91 (3)	74 (3)	123 (5)	1 (3)	24 (3)	14 (3)
C(16)	5410 (2)	3090 (2)	8630 (2)	91 (2)	132 (2)	176 (3)	14 (2)	−17 (2)	−12 (2)
C(17)	3184 (3)	4036 (2)	8278 (3)	93 (4)	78 (3)	125 (5)	0 (3)	10 (3)	−9 (3)
C(18)	1851 (3)	4109 (2)	7428 (3)	105 (4)	67 (3)	108 (4)	−4 (3)	26 (3)	4 (3)
C(19)	793 (2)	5077 (2)	7814 (3)	85 (3)	67 (3)	122 (4)	6 (2)	24 (3)	17 (3)
C(20)	1105 (3)	6102 (3)	9187 (3)	101 (4)	94 (3)	145 (5)	17 (3)	18 (4)	9 (3)
C(21)	82 (3)	6966 (3)	9525 (3)	155 (5)	104 (4)	150 (6)	36 (3)	43 (4)	5 (4)
C(22)	−1277 (3)	6838 (3)	8501 (4)	131 (5)	120 (4)	195 (6)	50 (3)	67 (4)	45 (4)
C(23)	−1599 (3)	5825 (3)	7131 (4)	102 (4)	124 (4)	181 (6)	21 (3)	20 (4)	45 (4)
C(24)	−569 (3)	4954 (2)	6796 (3)	108 (4)	85 (3)	140 (5)	11 (3)	18 (4)	17 (3)

(b) Hydrogen atoms. Positional parameters are × 10^3.

	x	y	z	B		x	y	z	B
H(1)	536 (2)	375 (2)	581 (2)	4·4 (6)	H(10)	278 (2)	−85 (2)	271 (2)	3·4 (6)
H(2)	613 (3)	377 (2)	337 (3)	6·2 (8)	H(17)	358 (2)	459 (2)	920 (2)	3·5 (6)
H(3)	567 (3)	195 (2)	111 (3)	6·8 (8)	H(18)	161 (2)	348 (2)	648 (2)	2·7 (5)
H(4)	418 (2)	15 (2)	129 (3)	5·1 (7)	H(20)	196 (2)	621 (2)	989 (2)	3·8 (6)
H(5)	125 (2)	−197 (2)	402 (3)	5·9 (7)	H(21)	29 (2)	761 (2)	42 (2)	4·0 (6)
H(6)	32 (3)	−192 (2)	636 (3)	6·5 (8)	H(22)	−202 (2)	747 (2)	869 (2)	4·6 (6)
H(7)	98 (2)	−28 (2)	870 (3)	5·3 (7)	H(23)	−250 (2)	583 (2)	641 (3)	5·9 (7)
N(8)	247 (2)	148 (2)	864 (2)	2·9 (5)	H(24)	−78 (2)	434 (2)	583 (2)	2·6 (5)

measured at both ends of the scan with ω displaced 1·0° from the $K\alpha$ peak. Two reflections $2\bar{1}1$ and $1\bar{3}1$, were too intense to be properly measured and were not included in the data set. In other respects, the data collection was similar to that for ASK.

For both ASK and ABSK, the net intensity, I (relative to a 1·0° min^{-1} scan rate), and its estimated standard deviation, $\sigma(I)$, were calculated as follows: $I = S(P-B_1-B_2)$; $\sigma(I)=S(P+B_1+B_2)^{1/2}$. Absorption corrections were not made. Conversion to structure amplitudes was completed with the application of Lorentz and polarization factors. Values of $\sigma(F_o)$ were derived directly from $\sigma(I)$ taking into account the various corrections that were made.

Structure solutions and refinements

The structure of ASK was determined in a straightforward manner from a Patterson synthesis. The orientation of the anthracene ring was readily deduced from the intramolecular C–C vectors; the position of this moiety in the unit cell was determined from the large intermolecular C–C peak which results from the summing of vectors between two anthracene rings related by a center of symmetry. A Fourier map, phased with the anthracene moiety, led to the location of the remaining non-hydrogen atoms.

The solution of the ABSK structure proved more difficult. The Patterson synthesis appeared to show the

Table 3. *Atomic coordinates and thermal parameters for ABSK*

(*a*) Non-hydrogen atoms. Positional and thermal parameters are × 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1*A*)	2294 (3)	−469 (3)	1740 (4)	94 (4)	83 (4)	96 (5)	13 (3)	28 (4)	47 (4)
C(2*A*)	3352 (3)	−738 (3)	1290 (4)	83 (4)	77 (4)	118 (5)	12 (3)	18 (4)	42 (4)
C(3*A*)	3323 (3)	−797 (3)	−66 (4)	85 (4)	85 (4)	142 (6)	16 (3)	51 (4)	51 (4)
C(4*A*)	2226 (3)	−585 (3)	−920 (4)	99 (5)	84 (4)	106 (5)	21 (3)	52 (4)	46 (4)
C(9*A*)	36 (3)	58 (3)	1350 (3)	78 (4)	55 (3)	66 (4)	0 (3)	23 (4)	26 (3)
C(13*A*)	1127 (3)	−240 (3)	882 (3)	74 (4)	55 (3)	85 (5)	7 (3)	25 (4)	29 (3)
C(14*A*)	1085 (3)	−299 (3)	−497 (3)	72 (4)	54 (3)	79 (5)	3 (3)	29 (4)	23 (3)
C(15*A*)	46 (3)	41 (3)	2749 (3)	75 (4)	86 (4)	90 (5)	9 (3)	29 (4)	43 (4)
O(16*A*)	−145 (2)	−967 (2)	2640 (2)	191 (4)	86 (3)	135 (4)	−6 (3)	61 (3)	62 (3)
C(17*A*)	301 (3)	1217 (3)	4194 (4)	97 (4)	91 (4)	91 (5)	9 (3)	37 (4)	45 (4)
C(18*A*)	671 (3)	2326 (3)	4448 (4)	96 (4)	90 (4)	115 (5)	16 (3)	44 (4)	57 (4)
C(19*A*)	969 (3)	3549 (3)	5898 (4)	104 (5)	82 (4)	113 (6)	2 (3)	30 (4)	31 (4)
C(20*A*)	836 (4)	3677 (4)	7192 (4)	124 (5)	89 (4)	120 (6)	−4 (4)	34 (4)	26 (4)
C(21*A*)	1051 (4)	4856 (4)	8495 (5)	156 (6)	156 (6)	134 (7)	6 (5)	51 (5)	25 (5)
C(22*A*)	1409 (5)	5925 (4)	8497 (6)	227 (8)	95 (5)	193 (8)	8 (5)	40 (7)	−9 (6)
C(23*A*)	1578 (5)	5802 (4)	7235 (6)	272 (9)	91 (5)	228 (9)	−14 (5)	52 (8)	39 (6)
C(24*A*)	1360 (4)	4616 (4)	5945 (5)	186 (7)	84 (4)	162 (7)	−19 (4)	32 (5)	39 (5)
C(1*B*)	5097 (4)	2368 (3)	3318 (4)	142 (5)	83 (4)	125 (6)	14 (4)	82 (5)	44 (4)
C(2*B*)	6183 (4)	1914 (4)	3814 (4)	163 (6)	83 (4)	182 (7)	30 (4)	118 (6)	53 (5)
C(3*B*)	7272 (4)	2707 (4)	5131 (5)	119 (5)	97 (5)	198 (7)	22 (4)	80 (5)	58 (5)
C(4*B*)	7220 (4)	3939 (4)	5913 (4)	107 (5)	110 (5)	129 (6)	−6 (4)	42 (5)	45 (5)
C(9*B*)	3938 (3)	4207 (3)	3675 (3)	110 (5)	85 (4)	96 (5)	−4 (3)	59 (4)	38 (4)
C(13*B*)	5040 (3)	3705 (3)	4148 (3)	117 (5)	68 (4)	94 (5)	1 (3)	63 (4)	28 (4)
C(14*B*)	6124 (3)	4498 (3)	5488 (3)	93 (4)	72 (4)	99 (5)	−3 (3)	45 (4)	33 (4)
C(15*B*)	2769 (3)	3337 (3)	2226 (4)	118 (5)	77 (4)	115 (4)	−4 (3)	53 (4)	29 (4)
O(16*B*)	1790 (2)	3015 (2)	2320 (3)	139 (4)	156 (3)	152 (4)	−51 (3)	74 (3)	35 (3)
C(17*B*)	2890 (4)	2915 (3)	734 (4)	105 (5)	90 (4)	93 (5)	−12 (3)	32 (4)	26 (4)
C(18*B*)	3945 (3)	3270 (3)	578 (4)	103 (5)	83 (4)	117 (5)	22 (3)	51 (4)	52 (4)
C(19*B*)	4121 (3)	2823 (3)	−895 (4)	104 (5)	82 (4)	113 (6)	2 (3)	30 (4)	31 (4)
C(20*B*)	3308 (4)	1816 (4)	−2267 (4)	104 (5)	182 (6)	105 (6)	39 (4)	42 (4)	71 (5)
C(21*B*)	3549 (5)	1459 (6)	−3589 (5)	164 (7)	286 (8)	112 (6)	101 (6)	51 (5)	103 (6)
C(22*B*)	4579 (6)	2098 (7)	−3560 (7)	312 (11)	357 (11)	308 (12)	210 (9)	242 (10)	279 (10)
C(23*B*)	5401 (6)	3088 (5)	−2207 (7)	298 (10)	221 (8)	402 (13)	130 (7)	268 (10)	232 (9)
C(24*B*)	5189 (4)	3461 (4)	−863 (5)	177 (6)	124 (5)	269 (9)	58 (4)	147 (6)	124 (6)

(*b*) Hydrogen atoms. Positional parameters are × 10^3.

	x	y	z	B		x	y	z	B
H(1*A*)	226 (2)	−48 (2)	258 (3)	3·9 (7)	H(1*B*)	423 (3)	163 (3)	220 (4)	7·5 (9)
H(2*A*)	428 (3)	−76 (3)	206 (3)	5·2 (8)	H(2*B*)	615 (3)	100 (3)	322 (3)	4·6 (7)
H(3*A*)	429 (3)	−87 (3)	−28 (3)	6·4 (8)	H(3*B*)	811 (3)	232 (3)	546 (3)	4·7 (7)
H(4*A*)	219 (2)	−63 (2)	−186 (3)	2·9 (6)	H(4*B*)	786 (2)	438 (2)	668 (2)	1·2 (6)
H(17*A*)	14 (3)	113 (3)	496 (3)	4·9 (8)	H(17*B*)	215 (2)	240 (2)	−11 (3)	3·7 (7)
H(18*A*)	90 (3)	238 (3)	369 (3)	6·2 (9)	H(18*B*)	484 (3)	399 (2)	164 (3)	4·6 (7)
H(20*A*)	64 (3)	299 (3)	726 (3)	4·8 (8)	H(20*B*)	264 (3)	141 (2)	−217 (3)	4·4 (7)
H(21*A*)	86 (3)	487 (3)	930 (3)	6·1 (9)	H(21*B*)	304 (3)	90 (3)	−437 (3)	4·3 (8)
H(22*A*)	164 (4)	678 (4)	947 (4)	10·2 (1·2)	H(22*B*)	455 (4)	158 (3)	−463 (4)	10·1 (1·2)
H(23*A*)	207 (4)	666 (4)	739 (5)	12·9 (1·4)	H(23*B*)	628 (4)	358 (3)	−213 (4)	9·7 (1·1)
H(24*A*)	126 (3)	449 (3)	490 (4)	8·8 (1·1)	H(24*B*)	584 (3)	411 (3)	19 (4)	6·9 (1·0)

orientation of the anthracene ring but no satisfactory intermolecular peak could be found. At this point, a set of normalized structure amplitudes was calculated; the statistics indicated that the space group was centrosymmetric, $P\bar{1}$. Attempts to solve the structure by direct methods led to two types of centrosymmetric solutions; phasing was carried out both by hand computations and by computerized procedures (*MULTAN*). The first type placed the anthracene rings parallel to each other across the center of symmetry with a perpendicular distance between the rings of about 3·5 Å. While solutions of this type looked reasonable, subsequent Fourier maps failed to reveal the locations of the other atoms. The second type placed the center of one anthracene ring at the center of symmetry but showed little else. The orientation of the anthracene ring in all of the E maps was, however, consistent with that found in the Patterson synthesis.

It was still possible of course that the space group was $P1$, the E statistics being biased by the symmetry of the molecule and the presence of a large number of planar rings. The structure was finally solved by assuming the space group to be $P1$ and placing one anthracene ring at the origin with the orientation suggested by the Patterson map (the position of the center of this ring in the unit-cell is arbitrary). This moiety sufficiently phased the structure amplitudes to locate several atoms in the two styryl keto groups. Fourier maps eventually revealed the second anthracene ring, in quite a different orientation, centered about the coordinates $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The space group was thus determined to be $P\bar{1}$, the asymmetric unit consisting of one-half of each of the two molecules which straddle centers of symmetry at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ respectively. An additional Fourier map then showed the positions of the remaining non-hydrogen atoms.

Refinement of the structures by the full-matrix least-squares method was carried out using only those reflections for which $I > 3\sigma(I)$: for ASK, 2184 reflections; for ABSK, 2439 reflections. Weights were assigned as $1/\sigma^2(F_o)$. Difference maps were used to locate the hydrogen atoms. Refinement of all positional and thermal (anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms) parameters converged at the following agreement indices: ASK, $R = 0{\cdot}046$ and $R_w = 0{\cdot}026$ (281 variables); ABSK, $R = 0{\cdot}052$ and $R_w = 0{\cdot}036$ (395 variables); where $R = (\sum||F_o| - |F_c||/\sum|F_o|)$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.* The average shift of the positional parameters in the final cycle of least squares was $0{\cdot}05\sigma$ for ASK and $0{\cdot}2\sigma$ for ABSK. The largest peaks in the final difference maps were less than 0·23 e Å^{-3}. Extinction did not prove to be a problem. The final positional and thermal parameters are given in Tables 2 and 3 for ASK and ABSK respectively.

For carbon and oxygen, the atomic scattering factors of Cromer & Waber (1965) were used; those of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms. Programs used in this study in-

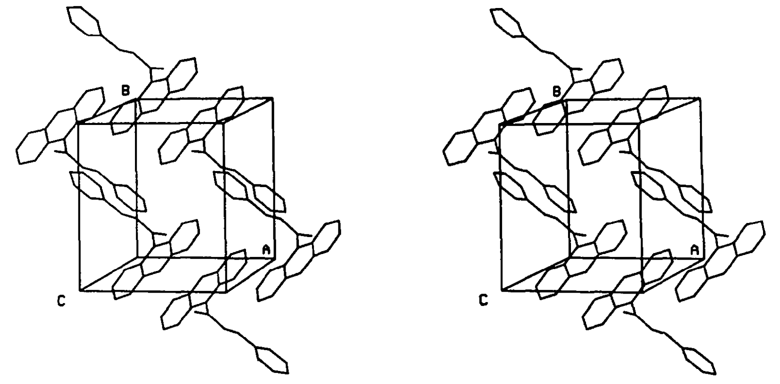


Fig. 1. Packing diagram for ASK.

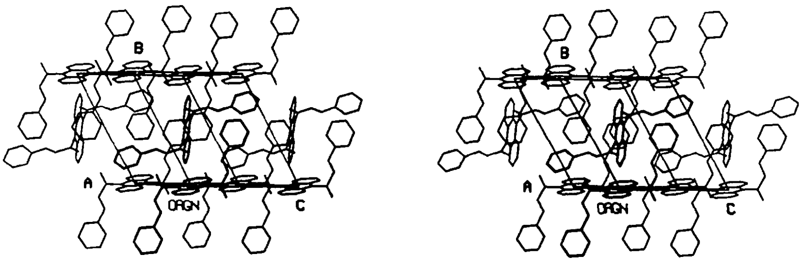


Fig. 2. Packing diagram for ABSK.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30856 (37 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Bond distances* (Å) *and angles* (°) *for ASK and ABSK*

Chemically equivalent bonds and angles for ASK are bracketed together.

	ASK	ABSK *A*	ABSK *B*
C(1)—C(2)	1·357 (4)	1·357 (5)	1·358 (6)
C(7)—C(8)	1·350 (4)		
C(1)—C(13)	1·423 (3)	1·425 (5)	1·447 (5)
C(8)—C(12)	1·423 (3)		
C(2)—C(3)	1·412 (5)	1·419 (6)	1·411 (7)
C(6)—C(7)	1·416 (5)		
C(3)—C(4)	1·346 (5)	1·361 (5)	1·334 (6)
C(5)—C(6)	1·340 (3)		
C(4)—C(14)	1·423 (4)	1·430 (5)	1·420 (6)
C(5)—C(11)	1·417 (3)		
C(9)—C(13)	1·408 (3)	1·402 (4)	1·397 (5)
C(9)—C(12)*	1·404 (3)	1·396 (5)	1·405 (5)
C(10)—C(14)	1·389 (3)		
C(10)—C(11)	1·388 (3)		
C(13)—C(14)	1·428 (3)	1·440 (5)	1·419 (5)
C(11)—C(12)	1·433 (3)		
C(9)—C(15)	1·508 (3)	1·520 (5)	1·536 (5)
C(15)—O(16)	1·214 (3)	1·215 (4)	1·204 (4)
C(15)—C(17)	1·458 (3)	1·451 (5)	1·474 (6)
C(17)—C(18)	1·325 (4)	1·314 (5)	1·334 (5)
C(18)—C(19)	1·471 (3)	1·476 (6)	1·476 (6)
C(19)—C(20)	1·385 (4)	1·381 (6)	1·386 (6)
C(20)—C(21)	1·367 (4)	1·385 (7)	1·379 (7)
C(21)—C(22)	1·378 (4)	1·396 (8)	1·382 (9)
C(22)—C(23)	1·377 (4)	1·366 (9)	1·372 (11)
C(23)—C(24)	1·376 (4)	1·384 (8)	1·382 (10)
C(19)—C(24)	1·378 (3)	1·379 (6)	1·413 (6)
C(2)—C(1)—C(13)	120·5 (3)	121·8 (4)	119·7 (4)
C(7)—C(8)—C(12)	121·3 (3)		
C(1)—C(2)—C(3)	121·5 (3)	120·3 (4)	122·1 (4)
C(6)—C(7)—C(8)	120·4 (3)		
C(2)—C(3)—C(4)	119·8 (3)	119·8 (3)	118·5 (4)
C(5)—C(6)—C(7)	120·5 (3)		
C(3)—C(4)—C(14)	121·1 (3)	122·1 (4)	123·3 (4)
C(6)—C(5)—C(11)	121·2 (3)		
C(1)—C(13)–C(14)	117·9 (2)	118·4 (3)	118·1 (3)
C(8)—C(12)–C(11)	117·7 (2)		
C(1)—C(13)–C(9)	122·6 (2)	122·2 (3)	121·3 (3)
C(8)—C(12)–C(9)	123·0 (2)		
C(9)—C(13)–C(14)	119·5 (2)	119·4 (3)	120·5 (3)
C(9)—C(12)–C(11)	119·2 (2)		
C(4)—C(14)–C(10)	121·9 (2)	122·5 (3)	123·3 (4)
C(5)—C(11)–C(10)	122·1 (2)		
C(4)—C(14)–C(13)	119·2 (2)	117·6 (3)	118·1 (3)
C(5)—C(11)–C(12)	118·9 (2)		
C(10)*–C(14)–C(13)	118·9 (2)	119·9 (3)	118·5 (3)
C(10)—C(11)–C(12)	119·0 (2)		
C(12)—C(9)—C(13)	120·9 (2)	120·7 (3)	121·0 (3)
C(11)—C(10)–C(14)	122·5 (2)		
C(12)*–C(9)—C(15)	120·2 (2)	119·8 (3)	119·1 (3)
C(13)—C(9)—C(15)	118·8 (2)	119·4 (3)	120·0 (3)
C(9)—C(15)–O(16)	119·6 (2)	119·1 (3)	120·4 (3)
C(9)—C(15)–C(17)	119·7 (2)	119·9 (3)	117·9 (3)
O(16)—C(15)–C(17)	120·7 (2)	121·0 (3)	121·7 (4)
C(15)—C(17)–C(18)	125·2 (2)	124·4 (4)	123·6 (4)
C(17)—C(18)–C(19)	128·1 (2)	126·9 (4)	124·9 (4)
C(18)—C(19)–C(20)	122·3 (2)	123·1 (3)	123·1 (3)
C(18)—C(19)–C(24)	119·2 (2)	118·3 (4)	117·0 (3)
C(20)—C(19)–C(24)	118·5 (2)	118·6 (4)	119·9 (4)
C(19)—C(20)–C(21)	120·7 (2)	120·8 (4)	119·1 (4)
C(20)—C(21)–C(22)	120·6 (2)	119·5 (5)	120·9 (5)
C(21)—C(22)–C(23)	119·3 (3)	120·0 (5)	120·5 (7)
C(22)—C(23)–C(24)	120·0 (3)	119·6 (5)	119·8 (6)
C(23)—C(24)–C(19)	121·0 (2)	121·4 (5)	119·7 (5)

* C(10) for ABSK is C(9′); C(12) is C(14′).

clude the following: *MULTAN*, by P. Main, M. M. Woolfson, and G. Germain; *RFOUR* (Fourier synthesis), by S. T. Rao, modified by R. E. Davis; *NUCLS* (full-matrix least-squares refinement), *ORFLS* as modified by J. A. Ibers; *DAESD* (distances, angles, and their estimated standard deviations), by D. R. Harris, modified by R. E. Davis; and *ORTEP*, by C. K. Johnson.

Discussion

Figs. 1 and 2 are packing diagrams for ASK and ABSK respectively and show two interesting features. First, the packing in ASK is more efficient because the anthracene ring systems are parallel, accounting for the greater density of ASK. This may also indicate why ABSK prefers to include solvent molecules in crystals obtained from solutions; it could undoubtedly pack in a more efficient manner. The second feature noted in the packing diagrams is the overall molecular geometry of the two compounds. The structures are sim-

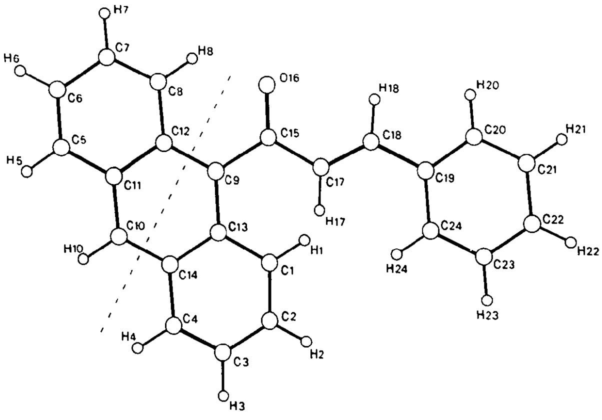


Fig. 3. Atom-numbering scheme for ASK and ABSK. The dashed line represents the fact that only half of the atoms of the two molecules of ABSK need to be numbered since each molecule sits on a center of symmetry.

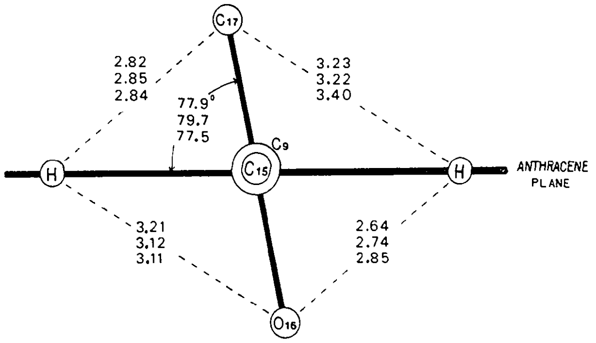


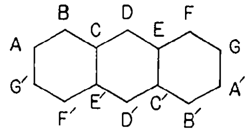
Fig. 4. Dihedral angles [anthracene ring to keto group consisting of C(9), C(15), O(16) and C(17)] and intramolecular contacts (Å) between the keto group and the hydrogen atoms at the 1 and 8 positions of the anthracene ring. Top to bottom, the values listed are for ASK, ABSK *A*, and ABSK *B*, respectively.

ilar in that the styryl-keto group, although reasonably planar as one might expect for a conjugated π system, is rotated by nearly 80° from the plane of the anthracene ring.

The bond distances and angles for ASK and ABSK (molecules *A* and *B*) are listed in Table 4 with the atoms numbered as shown in Fig. 3. Although the individual values are not listed, the average C–H distance is about 0·95 Å with no C–C–H angle deviating from 120° by more than 9°.

With one exception, all the bond lengths of the three styryl-keto groups agree to within two estimated standard deviations. The bond angles show considerable scatter, however, which may reflect the different environments of the groups; there appears to be no other way to explain the angular differences in ABSK molecules *A* and *B* which are chemically equivalent. Differences in packing have also affected the planarity of the styryl-keto groups; a mean-plane calculation through the entire group gives average deviations of 0·02, 0·05, and 0·07 Å for ASK, ABSK *A*, and ABSK *B*, respectively.

Focusing on the anthracene ring, a comparison of the 'substituted' with the 'unsubstituted' half of ASK revealed some differences in bond lengths and angles which eventually led to the production of Table 5. The question which Table 5 attempts to answer is: what differences in the geometry of the anthracene ring can be expected when substitution at the 9 and 10 positions takes place? Assuming *mmm* symmetry for all anthracene rings, except that of ASK where *mm* symmetry is used to divide the molecule into substituted and unsubstituted halves, the table lists average bond distances and angles for three studies of anthracene, average values for 9,10-substituted anthracenes where the carbon atom bonding to the ring is sp^2 hybridized on one hand and sp^3 hybridized on the other, and the average values for ASK and ABSK. The atom-labeling scheme is:



While the number of structures in the sample is small and most of the differences are not large enough to be statistically meaningful, substitution does appear to cause some consistent changes in the ring geometry as evidenced by a comparison of the average anthracene structure with the averages of the 9,10-substituted structures. The effect is most notable at the point of substitution, atom *D*, where bond length *CD* is found to increase while angle *CDE* decreases. This effect is larger when an sp^3-carbon bonds to the anthracene ring, presumably because of intramolecular steric interactions with the neighboring hydrogen atoms at positions 1 and 8 of the ring. In addition, small decreases in distances *AB* and *AG′* and 1° changes in angles *ABC* and *BCE′* can be noted. That these changes are not necessarily observed or observed to be opposite in sign when comparing the substituted with the unsubstituted half of ASK may be a reflection of the asymmetry of the substitution; even here, however, a lengthening of *CD* and a decrease in *CDE* with substitution can be readily noted. A comparison of the substituted half of ASK with ABSK reveals differences which are less than two estimated standard deviations and hence statistically insignificant.

The planarity of the anthracene ring is another important aspect of the structures since it is conceivable that substitution could cause the ring to be non-planar.

Table 5. *A comparison of some average bond distances* (Å) *and angles* (°) *for anthracene and* 9,10-*substituted anthracenes*

mmm symmetry for the anthracene moiety has been assumed throughout with the exception of the ring in ASK where *mm* symmetry has been assumed. The quantities in parentheses represent deviations from the anthracene average value.

	Average anthracene*	ASK		ABSK	Average sp^2 9,10-substituted†	Average sp^3 9,10-substituted‡
		Unsubstituted	Substituted			
AB	1·367	1·343	1·354	1·353	1·354 (−0·013)	1·354 (−0·013)
BC	1·433	1·420	1·423	1·431	1·432 (−0·001)	1·435 (+0·002)
CD	1·399	1·389	1·406	1·400	1·402 (+0·003)	1·409 (+0·010)
AG′	1·419	1·414		1·415	1·413 (−0·006)	1·406 (−0·013)
CE′	1·433	1·431		1·430	1·438 (+0·005)	1·435 (+0·002)
G′AB	120·8	120·9	120·9	120·2	120·4 (−0·4)	120·5 (−0·3)
ABC	120·3	121·2	120·9	121·8	121·4 (+1·1)	121·5 (+1·2)
BCE′	118·9	119·1	117·8	118·1	118·0 (−0·9)	117·9 (−1·0)
BCD	121·7	122·0	122·8	122·4	122·2 (+0·5)	121·8 (+0·1)
E′CD	119·5	119·0	119·4	119·6	119·8 (+0·3)	120·3 (+0·8)
CDE	121·0	122·5	120·9	120·9	120·5 (−0·5)	119·4 (−1·6)

* Average of three structural studies of anthracene: Cruickshank (1956); Mason (1964); and Lehmann & Pawley (1972), a neutron diffraction study of perdeuteroanthracene. The bond distances and angles used were those uncorrected for thermal libration.

† Average of the values for ABSK and 9,10-diphenylanthracene (Korp & Simonsen, 1974).

‡ Average values of three 9,10-substituted anthracene compounds recently studied: 9,10-dimethylanthracene, Iball & Low (1974); 9,10-bis(chloromethyl)anthracene, Gabe & Glusker (1971); and 10-methyl-9-{[(2-chloroethyl)thio]methyl}anthracene, Glusker & Zacharias (1972).

Table 6 lists the deviations from the best plane calculated for the anthracene ring in ASK and the two rings in ABSK. Viewed overall, the deviations are rather small and no general trend can be seen even for the two crystallographically independent rings in ABSK. The atom bound to the ring, C(15), is found to deviate from the plane, 0·023 and 0·087 Å for the chemically equivalent *A* and *B* molecules of ABSK. Again, packing forces must be invoked to explain the difference.

Table 6. *Deviations* (Å) *from the least-squares mean plane of the anthracene rings of ASK and ABSK*

(*a*) Atoms used in the calculation of the plane

	ASK	ABSK *A*	ABSK *B*
C(1)	−0·013	0·003	0·008
C(2)	−0·010	−0·006	−0·010
C(3)	0·001	−0·007	0·004
C(4)	0·019	0·004	0·007
C(5), C(1′)	−0·021	−0·003	0·008
C(6), C(2′)	−0·012	0·006	0·010
C(7), C(3′)	0·015	0·007	−0·004
C(8), C(4′)	0·021	−0·004	−0·007
C(9)	−0·005	0·000	0·015
C(10), C(9′)	0·009	0·000	−0·015
C(11), C(13′)	−0·006	−0·012	−0·016
C(12), C(14′)	−0·006	−0·013	−0·002
C(13)	−0·001	0·012	0·016
C(14)	0·011	0·013	0·002
(*b*) Other atoms			
C(15)	0·086	0·087	0·023
O(16)	1·132	1·161	−0·987
C(17)	−1·088	−1·109	1·299

It was pointed out earlier that the styryl-keto group in both structures is rotated nearly 80° out of the plane of the anthracene ring. A closer view of the situation is shown in Fig. 4 which gives the dihedral angles, anthracene plane to keto-group plane, for the various molecules. The agreement among the three values is surprisingly good; the average value is 78·4° which implies that π bonding between the anthracene ring and the styryl-keto group is not possible for either compound. This figure further records the C(17)···H and O(16)···H intramolecular contacts, all of which are greater than the sum of the van der Waals radii for these atoms. This would indicate that steric interactions between the styryl-keto group and the anthracene ring are minimal.

With no steric interactions and no π bonding between the anthracene ring and the styryl-keto group, and only small differences in the geometry of the anthracene rings, it is not possible from the crystallographic results to explain why the disproportionation of ASK to form anthracene and ABSK is thermodynamically favored. With the keto group rotated by 80° from the anthracene plane, steric interactions between almost any acyl group and the anthracene ring will always be minimal; thus, there is a possibility that steric requirements cannot be used to account for the fact that some 9-acetylanthracenes rearrange and others disproportionate. An X-ray study of 9-acetylanthracene is at present under consideration and will be highly elucidating with respect to steric interactions. One speculation at this point is that the chemical differences are perhaps related to the stability of the carbonium ion. Carbonium ions which can delocalize the positive charge over a conjugated π system yield the thermodynamically favored disproportionation products, while those lacking this delocalization ability are relatively unstable and yield the kinetically favored rearrangement products.

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