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Structures and Photochemical Reactions of 1-(9-Anthryl)-2-aroylethylenes: Competing *cis–trans* Isomerization and Skeletal Rearrangement

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Abstract

(*Z*)-3-(9-Anthryl)-1-phenylpropenone, *cis*-(I), $C_{23}H_{16}O$, $M_r = 308.38$, orthorhombic, $P2_12_12_1$, $a = 14.992\,(3)$, $b = 19.124\,(4)$, $c = 5.614\,(1)$ Å, $V = 1609.4\,(6)$ Å^3, $Z = 4$, $D_x = 1.273$ g cm^{-3}, $\mu = 0.071$ mm^{-1}, $F(000) = 648$, $R = 0.061$ for 1101 observed reflections; (*Z*)-2-(9-anthrylmethylene)-1-indanone, *cis*-(III), $C_{24}H_{16}O$, $M_r = 320.40$, monoclinic, $P2_1/a$, $a = 11.641\,(5)$, $b = 13.914\,(10)$, $c = 10.399\,(6)$ Å, $\beta = 102.71\,(4)°$, $V = 1643.1\,(16)$ Å^3, $Z = 4$, $D_x = 1.295$ g cm^{-3}, $\mu = 0.072$ mm^{-1}, $F(000) = 672$, $R = 0.060$ for 2321 observed reflections; (*Z*)-2-(9-anthrylmethylene)-1-tetralone, *cis*-(IV), $C_{25}H_{18}O$, $M_r = 334.39$, monoclinic, $P2_1/c$, $a = 9.106\,(4)$, $b = 25.977\,(9)$, $c = 7.478\,(2)$ Å, $\beta = 96.76\,(5)°$, $V = 1756.6\,(11)$ Å^3, $Z = 4$, $D_x = 1.264$ g cm^{-3}, $\mu = 0.070$ mm^{-1}, $F(000) = 704$, $R = 0.070$ for 1594 observed reflections; (*E*)-2-(9-anthrylmethylene)-1-tetralone, *trans*-(IV), $C_{25}H_{18}O$, $M_r = 334.39$, monoclinic, $P2_1/c$, $a = 12.032\,(2)$, $b = 13.608\,(3)$, $c = 10.829\,(3)$ Å, $\beta = 95.78\,(2)°$, $V = 1764.1\,(7)$ Å^3, $Z = 4$, $D_x = 1.259$ g cm^{-3}, $\mu = 0.070$ mm^{-1}, $F(000) = 704$, $R = 0.055$ for 1985 observed reflections. *cis*-(I), *cis*-(III) and *cis*-(IV) exist in a conformation similar to each other, in which the anthracene plane forms a large dihedral angle [75.5 (3), 64.5 (1) and 67.2 (2)°, respectively] with the ethylene plane. These com-

pounds rapidly undergo photochemical *cis–trans* isomerization in solution, while irradiation of *cis*-(I) in the solid state almost exclusively afforded an intramolecular [4 + 2] cyclization product, suggesting that the isomerization would be inhibited by crystal-lattice constraints. *cis*-(IV) also underwent [4 + 2] cyclization in the solid state, while in the case of *cis*-(III) only *cis–trans* isomerization was observed both in solution and in the solid state. A comparison of the molecular structures of *cis*-(I), -(III) and -(IV) suggested that the C(6)···O distance, where a new bond would be formed in the cyclization process, should be related to the photochemical reactivity.

Introduction

It was reported that 3-(9-anthryl)-1-phenylpropenone (I) underwent photochemical skeletal rearrangement into a furano-annelated 5*H*-dibenzo[*a*,*d*]cycloheptene (II) through [4 + 2] cycloaddition involving the conjugated dienone moiety in a benzene solution (Becker, Becker, Sandros & Andersson, 1985). This photochemical transformation is quite inefficient in solution due to competition with energy-wasting *cis–trans* isomerization. In general, crystalline-state reactions tend to be controlled by packing arrangements of the reacting molecules and therefore selectivity among competing reaction pathways will differ from that observed in solution. In the case of (I) it is

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expected that cis–trans isomerization which accompanies large atomic movement around the olefinic C=C bond would be inhibited to some extent, resulting in selective formation of the cyclization product in the solid state. In fact, when the crystals of cis-(I) were irradiated, the [4 + 2] cycloaddition occurred preferentially, compared to cis–trans isomerization, although the photochemical conversion proceeded very slowly in the solid state. In order to clarify the relationship between the structure of the enones and reactivity of [4 + 2] cyclization, and to reveal the effects of crystal lattice on the selectivity of cyclization versus cis–trans isomerization, we chose compound (I) and its cyclic derivatives, 2-(9-anthrylmethylene)-1-indanone (III) and 2-(9-anthrylmethylene)-1-tetralone (IV), and investigated the photochemical behaviour of both trans and cis isomers, both in solution and the solid state. Recently D'Auria, D'Ononfrio & Vantaggi (1990) reported a similar type of photochemical rearrangement for a 2-methylene-1-tetralone derivative in solution. The present paper describes the crystal structures of cis-(I), cis-(III), cis-(IV) and trans-(IV) and the relationship between structure and photochemical reactivity.
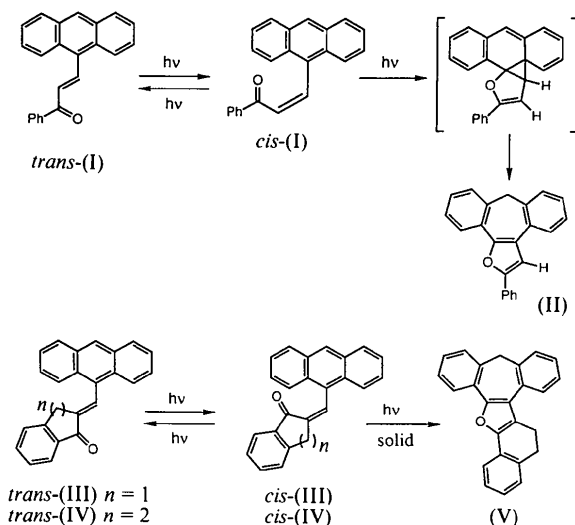
Experimental

(E)-3-(9-Anthryl)-1-phenylpropenone [trans-(I)], (E)-2-(9-anthrylmethylene)-1-indanone [trans-(III)] and (E)-2-(9-anthrylmethylene)-1-tetralone [trans-(IV)] were synthesized from 9-anthraldehyde and appropriate ketones by the method of Russell & Happoldt (1942). cis isomers were obtained by irradiation of the trans isomers in ethanol followed by chromatographic separation. Photolysis was carried out with a 400 W high-pressure mercury lamp through a 330 nm cut-off filter (1 M KNO_3 aqueous solution)

at 293–298 K. Solid-state photochemical reactions were carried out in KBr pellets containing 2%(w/w) sample and the resulting reaction mixture was extracted from the pellets with CDCl_3. Yields of the photoproducts were determined based on integration ratios of ^{1}H NMR signals. ^{1}H NMR spectra (270 MHz) were recorded on a JEOL JNM-GX270 spectrometer in benzene-d_6 or CDCl_3. Absorption spectra were recorded in cyclohexane using a Shimadzu UV-2200 spectrophotometer. Quantum yields in the solid state were measured at low conversion (< 3%) using a potassium ferrioxalate actinometer and HPLC analysis with Jasco Trirotar-IV apparatus.

Each single crystal of cis-(I), cis-(III), cis-(IV) and trans-(IV) was obtained by recrystallization from an ethanol solution. The intensity data were collected on a Rigaku AFC-5 diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71068$ Å) by ω–2θ scan technique with a scan width of (1.0 + 0.35tanθ)° at 293 K. Background counts were accumulated for 5 s before and after each scan. The intensities of three standard reflections were monitored every 50 reflections and no significant variation was observed. Data were corrected for Lorentz and polarization factors but not for absorption. The structures were solved by direct methods using MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least-squares methods on F with SHELX76 (Sheldrick, 1976). The H atoms were located from difference maps, except for cis-(III) where some H atoms were assigned at geometrically calculated positions and then refined. The final refinements were made with anisotropic and isotropic thermal parameters for non-H and H atoms, respectively. Details of data collection and structure refinement are summarized in Table 1. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1974, Vol. IV). Calculations were carried out on an IBM 4381-R24 computer at Ochanomizu University.

Results and discussion

The final atomic coordinates for non-H atoms are given in Table 2.* The molecular structures with the atomic numbering are shown in Fig. 1. Selected bond distances and angles are listed in Table 3, and some other structural parameters are given in Table 4. As is seen in Fig. 1, cis-(I), -(III) and -(IV) showed

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<div align="center">Table 1. Data collection and refinement parameters</div>

	cis-(I)	cis-(III)	cis-(IV)	trans-(IV)
Crystal size (mm)	0.4 × 0.1 × 0.1	0.3 × 0.25 × 0.2	0.4 × 0.15 × 0.05	0.35 × 0.3 × 0.2
Reflections for cell parameters				
No.	18	19	18	17
2θ range (°)	23-27	22-29	23-29	24-28
Intensity measurement				
$2\theta_{max}$ (°)	50	55	50	50
h	0-17	-16-16	-11-11	-14-14
k	0-21	0-20	0-30	0-16
l	-6-0	0-15	0-8	0-12
Scan speed [° min^{-1} (θ)]	4 ($2\theta < 35°$)	4	4 ($2\theta < 35°$)	4
	2 ($2\theta > 35°$)		2 ($2\theta > 35°$)	
Measured reflections	1687	3778	3337	3289
Unique reflections	1687	3778	2420	2676
Observed reflections	1101*	2321*	1594*	1985†
R_{int}	–		0.02	0.01
Structure refinement				
$(\Delta/\sigma)_{max}$	0.3	0.07	0.24	0.56
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.17/-0.20	0.22/-0.22	0.20/-0.21	0.32/-0.23
R	0.061	0.060	0.070	0.055
wR	0.066	0.068	0.073	0.062
Weighting scheme $1/[\sigma^2(F_o) + aF_o^2]$				
a value	0.0024	0.0018	0.0018	0.0020
No. of parameters	281	290	307	307

* Reflections with $F_o > 2\sigma(F_o)$ were considered observed.
† Reflections with $F_o > 3\sigma(F_o)$ were considered observed.

<div align="center">Table 2. Final atomic coordinates (× 10⁴) and equivalent thermal parameters (Å²) for non-H atoms</div>

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}		x	y	z	B_{eq}
cis-(I)					C(14)	2808 (3)	3874 (2)	8907 (3)	3.6 (1)
C(1)	4067 (5)	6819 (5)	3807 (18)	6.0 (2)	C(15)	4885 (3)	5842 (2)	8171 (3)	3.5 (1)
C(2)	3988 (6)	6293 (5)	2253 (19)	6.0 (2)	C(16)	4491 (2)	6700 (2)	7706 (3)	3.1 (1)
C(3)	4605 (7)	6235 (5)	366 (19)	6.4 (3)	C(17)	3298 (2)	6935 (2)	6901 (3)	3.1 (1)
C(4)	5289 (6)	6690 (4)	113 (16)	5.5 (2)	C(18)	3336 (2)	7950 (2)	6497 (3)	3.0 (1)
C(5)	5404 (4)	7249 (3)	1791 (13)	4.3 (2)	C(19)	2456 (3)	8486 (2)	5690 (3)	3.9 (1)
C(6)	6125 (4)	7723 (3)	1636 (13)	4.1 (2)	C(20)	2715 (3)	9407 (2)	5369 (3)	4.4 (1)
C(7)	6173 (4)	8288 (3)	3104 (11)	3.9 (2)	C(21)	3831 (3)	9784 (2)	5852 (3)	4.1 (1)
C(8)	6857 (5)	8810 (5)	3006 (16)	5.6 (2)	C(22)	4710 (3)	9261 (2)	6673 (3)	3.9 (1)
C(9)	6873 (6)	9343 (4)	4574 (20)	6.5 (3)	C(23)	4453 (2)	8327 (2)	6988 (3)	3.2 (1)
C(10)	6239 (6)	9417 (4)	6406 (18)	6.1 (2)	C(24)	5248 (3)	7595 (2)	7806 (3)	3.8 (1)
C(11)	5583 (5)	8946 (4)	6627 (16)	5.5 (2)	O	2460 (2)	6389 (1)	6584 (2)	4.4 (1)
C(12)	5526 (4)	8364 (3)	5005 (13)	4.3 (2)					
C(13)	4837 (4)	7876 (4)	5191 (14)	4.6 (2)	**cis-(IV)**				
C(14)	4768 (4)	7316 (3)	3613 (13)	4.0 (2)	C(1)	4624 (7)	2018 (2)	1685 (10)	5.1 (2)
C(15)	6820 (5)	7634 (4)	-282 (14)	5.5 (2)	C(2)	3851 (8)	1882 (3)	147 (11)	6.0 (2)
C(16)	7465 (5)	7165 (4)	-362 (13)	4.8 (2)	C(3)	4537 (8)	1621 (3)	-1174 (9)	5.9 (2)
C(17)	7653 (4)	6656 (4)	1604 (12)	4.0 (2)	C(4)	6001 (7)	1502 (2)	-926 (8)	4.7 (2)
C(18)	8166 (4)	6011 (3)	997 (11)	3.6 (1)	C(5)	6892 (6)	1624 (2)	713 (7)	4.1 (1)
C(19)	8164 (4)	5472 (4)	2633 (12)	3.8 (2)	C(6)	8409 (6)	1511 (2)	1047 (6)	3.5 (1)
C(20)	8619 (5)	4864 (4)	2251 (14)	4.6 (2)	C(7)	9228 (6)	1668 (2)	2665 (7)	3.8 (1)
C(21)	9108 (5)	4787 (4)	161 (15)	5.1 (2)	C(8)	10771 (7)	1573 (2)	3039 (8)	4.9 (2)
C(22)	9136 (5)	5318 (4)	-1516 (17)	5.1 (2)	C(9)	11574 (9)	1760 (3)	4532 (9)	5.8 (2)
C(23)	8652 (4)	5925 (4)	-1101 (12)	4.3 (2)	C(10)	10871 (9)	2053 (3)	5816 (9)	5.9 (2)
O	7389 (4)	6760 (3)	3596 (9)	6.2 (2)	C(11)	9406 (9)	2124 (2)	5567 (8)	5.1 (2)
					C(12)	8511 (7)	1941 (2)	3974 (7)	3.9 (2)
cis-(III)					C(13)	7006 (7)	2041 (2)	3642 (8)	4.5 (2)
C(1)	1890 (3)	3767 (2)	9609 (3)	4.6 (1)	C(14)	6176 (6)	1893 (2)	2051 (7)	4.0 (2)
C(2)	1505 (3)	4513 (3)	10225 (4)	5.2 (1)	C(15)	9209 (6)	1288 (2)	-383 (7)	4.0 (1)
C(3)	2024 (3)	5429 (3)	10185 (3)	4.7 (1)	C(16)	9064 (6)	821 (2)	-1120 (6)	3.9 (1)
C(4)	2888 (3)	5574 (2)	9522 (3)	3.9 (1)	C(17)	8064 (6)	424 (2)	-521 (7)	3.9 (1)
C(5)	3318 (2)	4810 (2)	8836 (3)	3.3 (1)	C(18)	7384 (6)	61 (2)	-1914 (7)	4.4 (2)
C(6)	4242 (2)	4922 (2)	8166 (3)	3.1 (1)	C(19)	6381 (8)	-308 (2)	-1441 (9)	5.4 (2)
C(7)	4662 (2)	4119 (2)	7581 (3)	3.4 (1)	C(20)	5690 (8)	-636 (2)	-2693 (11)	6.2 (2)
C(8)	5576 (3)	4186 (2)	6869 (3)	4.4 (1)	C(21)	5969 (8)	-596 (3)	-4484 (11)	5.9 (2)
C(9)	5971 (3)	3399 (3)	6316 (4)	5.1 (1)	C(22)	6942 (8)	-232 (3)	-4971 (8)	5.4 (2)
C(10)	5476 (3)	2483 (3)	6426 (4)	5.2 (1)	C(23)	7663 (6)	103 (2)	-3720 (7)	4.2 (1)
C(11)	4602 (3)	2389 (2)	7073 (3)	4.7 (1)	C(24)	8671 (7)	512 (2)	-4275 (8)	4.8 (2)
C(12)	4156 (3)	3191 (2)	7669 (3)	3.7 (1)	C(25)	9828 (7)	664 (3)	-2723 (8)	4.6 (2)
C(13)	3235 (3)	3099 (2)	8320 (3)	3.9 (1)	O	7815 (5)	394 (2)	1042 (5)	5.7 (1)

Table 2 (cont.)

	x	y	z	B_{eq}		x	y	z	B_{eq}
trans-(IV)					trans-(IV) (cont.)				
C(1)	-1432 (3)	894 (3)	9623 (3)	5.2 (1)	C(14)	-503 (2)	885 (2)	8913 (3)	4.1 (1)
C(2)	-1482 (3)	1520 (3)	10581 (3)	5.8 (1)	C(15)	2215 (2)	2305 (2)	8836 (3)	4.2 (1)
C(3)	-608 (3)	2177 (3)	10907 (3)	5.4 (1)	C(16)	3245 (2)	2163 (2)	9318 (3)	4.5 (1)
C(4)	301 (3)	2203 (2)	10261 (3)	4.4 (1)	C(17)	3992 (2)	3016 (2)	9629 (3)	4.3 (1)
C(5)	383 (2)	1563 (2)	9228 (2)	3.9 (1)	C(18)	4888 (2)	2892 (2)	10666 (3)	4.3 (1)
C(6)	1327 (2)	1562 (2)	8541 (2)	3.8 (1)	C(19)	5591 (3)	3684 (3)	10996 (3)	5.7 (1)
C(7)	1402 (2)	871 (2)	7584 (2)	4.0 (1)	C(20)	6416 (3)	3602 (3)	11973 (4)	6.9 (1)
C(8)	2336 (3)	824 (2)	6873 (3)	4.8 (1)	C(21)	6529 (3)	2732 (3)	12620 (4)	6.9 (1)
C(9)	2395 (3)	123 (3)	5988 (3)	5.8 (1)	C(22)	5842 (3)	1945 (3)	12309 (3)	5.8 (1)
C(10)	1537 (3)	-578 (3)	5743 (3)	6.0 (1)	C(23)	5004 (2)	2011 (2)	11325 (3)	4.5 (1)
C(11)	623 (3)	-537 (2)	6369 (3)	5.5 (1)	C(24)	4223 (3)	1165 (3)	11008 (3)	5.4 (1)
C(12)	511 (2)	183 (2)	7301 (3)	4.1 (1)	C(25)	3777 (3)	1159 (2)	9630 (3)	5.7 (1)
C(13)	-423 (3)	223 (2)	7956 (3)	4.6 (1)	O	3856 (2)	3792 (1)	9064 (2)	5.1 (1)

similar conformations. The anthracene moiety and ethylene plane are almost perpendicular with each other. The dihedral angle between the anthracene and ethylene planes of cis-(I) is comparable with that of cis-9-(β-styryl)anthracene (78.4°; Becker, Patrick & White, 1984), while the corresponding angles of cis-(III), cis-(IV) and trans-(IV) are a little smaller. In cis-(IV) the carbonyl plane is slightly rotated from the ethylene plane and the cyclohexene ring is puckered. On the other hand, in cis-(III) the 2-methylene-1-indanone moiety is almost planar and the sp^3-carbon, C(24), deviates only by 0.029 Å from the least-squares plane composed of C(16), C(17), C(18), C(19), C(20), C(21), C(22) and C(23). The torsion angle of C(6)—C(15)—C(16)—C(17) of cis-(III) is somewhat larger than that of cis-(I) or cis-(IV), indicating that the olefinic moiety of cis-(III) is somewhat sterically hindered. The structure parameters of trans-(IV) are similar to the corresponding values of cis-(IV) except for the configuration of the C=C double bond (Table 4).

Table 5 summarizes the product ratio of photochemical reactions of (I), (III) and (IV). When irradiated in benzene each trans isomer of (I), (III) and (IV) underwent cis–trans isomerization and a photostationary state was rapidly attained. After prolonged irradiation, (I) afforded the cyclization product (II) quantitatively, while (III) and (IV) gave no corresponding photoproduct. The absorption spectra of cis-(I), cis-(III) and cis-(IV) are similar to each other, exhibiting fine structure characteristics for the S_0–S_1 transition of the anthracene chromophore. According to Becker & Andersson (1983), conjugation of the substituent attached to the C=C double bond with the 9-vinylanthracene chromophore causes loss of fine structure in the absorption spectrum. As mentioned above, the anthracene plane makes a large dihedral angle with the enone moiety, which should decrease the conjugation and bring about the fine structure of the absorption spectrum. The similarity in the absorption spectrum of the three cis isomers suggests that the lack of reactivity for the cyclization of cis-(III) and cis-(IV) cannot be attri-

Table 3. Selected bond distances (Å) and angles (°)

cis-(I)
C(6)—C(15)	1.508 (11)	C(6)—C(15)—C(16)	127.4 (7)
C(15)—C(16)	1.319 (11)	C(15)—C(16)—C(17)	123.7 (7)
C(16)—C(17)	1.499 (10)	C(16)—C(17)—C(18)	117.8 (6)
C(17)—C(18)	1.492 (9)	C(16)—C(17)—O	121.0 (7)
C(17)—O	1.203 (9)	C(18)—C(17)—O	121.3 (6)

cis-(III)
C(6)—C(15)	1.482 (4)	C(6)—C(15)—C(16)	129.8 (3)
C(15)—C(16)	1.331 (4)	C(15)—C(16)—C(17)	127.2 (3)
C(16)—C(17)	1.492 (4)	C(15)—C(16)—C(24)	124.3 (3)
C(16)—C(24)	1.517 (5)	C(17)—C(16)—C(24)	108.3 (2)
C(17)—C(18)	1.477 (4)	C(16)—C(17)—C(18)	106.6 (2)
C(17)—O	1.223 (4)	C(16)—C(17)—O	127.1 (3)
C(18)—C(23)	1.390 (4)	C(18)—C(17)—O	126.2 (3)
C(23)—C(24)	1.507 (5)	C(17)—C(18)—C(19)	128.3 (3)
		C(17)—C(18)—C(23)	109.9 (2)
		C(18)—C(23)—C(24)	111.2 (3)
		C(22)—C(23)—C(24)	128.9 (3)
		C(16)—C(24)—C(23)	103.9 (3)

cis-(IV)
C(6)—C(15)	1.481 (8)	C(6)—C(15)—C(16)	128.3 (5)
C(15)—C(16)	1.334 (8)	C(15)—C(16)—C(17)	123.0 (5)
C(16)—C(17)	1.479 (7)	C(15)—C(16)—C(25)	122.7 (5)
C(16)—C(25)	1.511 (8)	C(17)—C(16)—C(25)	114.2 (5)
C(17)—C(18)	1.485 (8)	C(16)—C(17)—C(18)	116.8 (5)
C(17)—O	1.219 (7)	C(16)—C(17)—O	121.7 (5)
C(18)—C(23)	1.407 (8)	C(18)—C(17)—O	121.5 (5)
C(23)—C(24)	1.494 (8)	C(17)—C(18)—C(19)	119.2 (5)
C(24)—C(25)	1.525 (9)	C(17)—C(18)—C(23)	121.1 (5)
		C(18)—C(23)—C(24)	120.5 (5)
		C(23)—C(24)—C(25)	111.4 (5)
		C(16)—C(25)—C(24)	109.4 (5)

trans-(IV)
C(6)—C(15)	1.481 (4)	C(6)—C(15)—C(16)	128.2 (3)
C(15)—C(16)	1.310 (4)	C(15)—C(16)—C(17)	120.1 (3)
C(16)—C(17)	1.486 (4)	C(15)—C(16)—C(25)	125.2 (3)
C(16)—C(25)	1.532 (5)	C(17)—C(16)—C(25)	114.7 (3)
C(17)—C(18)	1.486 (4)	C(16)—C(17)—C(18)	117.3 (3)
C(17)—O	1.223 (4)	C(16)—C(17)—O	120.9 (3)
C(18)—C(19)	1.394 (5)	C(18)—C(17)—O	121.7 (3)
C(18)—C(23)	1.395 (4)	C(17)—C(18)—C(19)	118.8 (3)
C(23)—C(24)	1.504 (5)	C(17)—C(18)—C(23)	120.8 (3)
C(24)—C(25)	1.535 (5)	C(18)—C(23)—C(24)	120.9 (3)
		C(23)—C(24)—C(25)	112.0 (3)
		C(16)—C(25)—C(24)	107.9 (3)

buted to differences in the electronic nature of the S_1 state between cis-(I) and cis-(III) or cis-(IV).

When cis-(I) was irradiated in the solid state, (II) was preferentially formed and only a trace amount of trans-(I) was detected in the photolysate. As shown in Fig. 1, cis-(I) exists in the s-cis conformation in the

crystal and as a result, the distance of C(6)···O is as short as 2.86 Å, which is favourable for the photochemical cyclization. According to Becker *et al.* (1985), the quantum yield for formation of (II) from *cis*-(I) is 8×10^{-4} in benzene, while that for isomerization to *trans*-(I) is 0.10. In the solid state the quantum yield for formation of (II) from *cis*-(I) was 1.3×10^{-4} which was about one sixth of that obtained in solution. Zimmerman & Zuraw (1989)
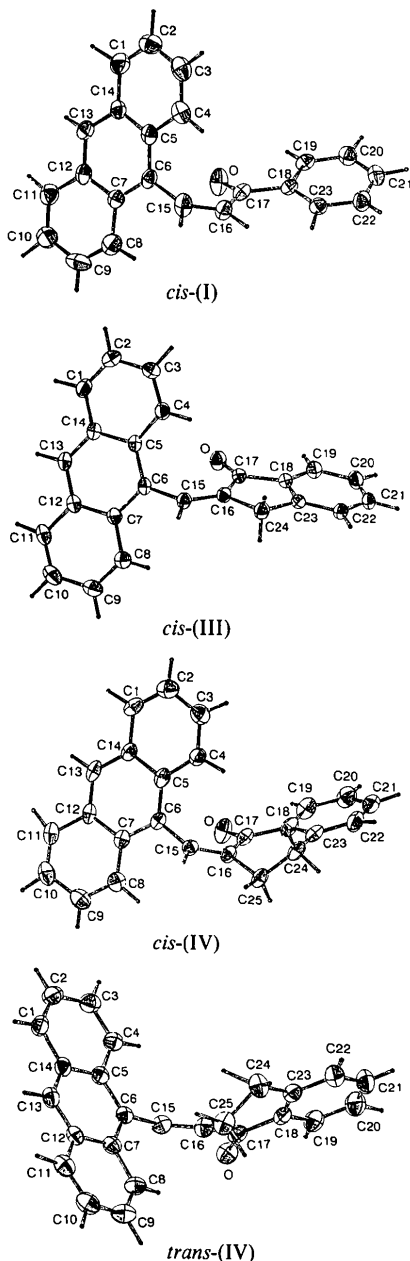

Fig. 1. *ORTEP* (Johnson, 1965) diagrams of *cis*-(I), *cis*-(III), *cis*-(IV) and *trans*-(IV) with atomic numbering. The thermal ellipsoids for non-H atoms are at 30% probability.

Table 4. *Comparison of some structural parameters among cis-(I), cis-(III), cis-(IV) and trans-(IV)*

	cis-(I)	cis-(III)	cis-(IV)	trans-(IV)
Distance (Å)				
C(6)···O	2.862 (9)	3.111 (4)	2.952 (7)	4.294 (3)
Dihedral angles (°)				
Anthryl–ethylene	75.5 (3)	64.5 (1)	67.2 (2)	64.8 (1)
Ethylene–carbonyl	39.3 (2)	2.6 (1)	31.7 (2)	28.4 (1)
Carbonyl–phenyl	14.9 (3)	4.2 (1)	2.6 (3)	1.8 (1)
C(6)—C(15)—C(16)—C(17)	−4.5 (13)	−7.9 (5)	−2.9 (9)	−175.3 (3)
C(17)—C(16)—C(25)—C(24)			56.0 (6)	54.9 (4)
C(23)—C(24)—C(25)—C(16)			−54.8 (6)	−54.6 (4)
C(18)—C(23)—C(24)—C(25)			28.0 (8)	29.5 (4)

Table 5. *Product ratio (%) of photochemical reactions of (I), (III) and (IV) in the solid state and in solution*

	Solid state[a]			Solution[b,c]		
	trans	cis	Cyclization product	trans	cis	Cyclization product
trans-(I)	90	–	10 (II)	8	69	23 (II)
cis-(I)	Trace	86	14 (II)			
trans-(III)	77	3	_[d]	32	68	_[e]
cis-(III)	89	11	–			
trans-(IV)	94	–	6(V)	93	7	–
cis-(IV)	8	85	6(V)			

Notes: (a) After 12 h irradiation in KBr pellets. (b) After 3.5 h irradiation in benzene-d_6. (c) The photostationary state of the *cis–trans* isomerization has been established. (d) An unidentified product was detected. (e) In methanol solution.

suggested the following interpretation for solid-state unimolecular-photochemical reactions, 'In cases where solid-state photochemistry differs from that in solution, the reaction which is energetically preferred in solution is inhibited by crystal lattice constraints, and a reaction process with a higher activation energy can proceed in the solid state'. This idea is true of the crystalline-state photochemical reaction of *cis*-(I). In the solid state, the isomerization of *cis*-(I) to *trans*-(I), which is energetically much more favoured than the cyclization into (II) in solution, is inhibited and as a result preferential formation of (II) is observed. On the other hand, irradiation of the crystals of *trans*-(I) afforded (II) in a comparable yield with irradiation of *cis*-(I), but *cis*-(I) which is considered as the immediate precursor of (II) was not detected in the photolysate. One explanation of the lack of *cis*-(I) is that (II) is formed directly from the excited state of *trans*-(I) by a one-photon process and not through the ground state of the *cis* isomer. Another, more likely, explanation is that at first *cis*-(I) is formed, then rapidly converted to (II) or *trans*-(I), since the crystalline lattice surrounding the *cis*-(I) molecule was destroyed during the transformation of *trans*-(I) to *cis*-(I) to give the *cis*-(I) molecule a larger reaction cavity.

As shown in Table 5, irradiation of *trans*-(III) or *cis*-(III) in the solid state gave no cyclization product and *cis*-(III) gave *trans*-(III) in rather high yield. The enlargement of angles C(15)—C(16)—C(17) and

C(16)—C(17)—O in cis-(III) causes the C(16)···O distance to be larger than that of cis-(I), and also of cis-(IV), as shown in Table 4, which seems to provide one of the reasons why cis-(III) is inactive for the photochemical cyclization. In the case of trans-(III), another photoproduct was yielded as well as a small amount of cis-(III). The product derived from trans-(III) could not be isolated because of its instability, but the ¹H NMR spectrum showed two singlets at δ 2.84 and 4.81 (integration ratio 2:1) and aromatic proton signals at δ 6.7–7.1, suggesting that the product may be an anthracene dimer formed by inter-molecular [4 + 4] cycloaddition. It is noteworthy that the solid-state photochemical behaviours of trans-(III) and cis-(III) are very different from each other in contrast with the photochemical reaction observed in solution where irradiation of both trans-(III) and cis-(III) gave a mixture with the same isomer ratio.

In the case of cis-(IV), solid-state photolysis caused both the cis–trans isomerization and the cyclization to give a fused furan-type product (V) which was unattainable in solution. A comparison of geometrical parameters (Table 3) in the enone moiety between cis-(IV) and cis-(I) indicated that C(6)—C(15) and C(16)—C(17) distances in cis-(IV) are a little shorter than the corresponding distances in cis-(I), while C(15)—C(16) in cis-(IV) is slightly longer than that in cis-(I). As for the bond angles around C(15), C(16) and C(17) no significant difference is observed. As a result, the C(6)···O distance in cis-(IV) is somewhat longer than that in cis-(I) but shorter than that in cis-(III) (Table 4). It seems that the difference of the C(6)···O distance among cis-(I), cis-(III) and cis-(IV) would, at least partly, cause the different tendencies in the solid-state photochemical reactions of these three compounds.
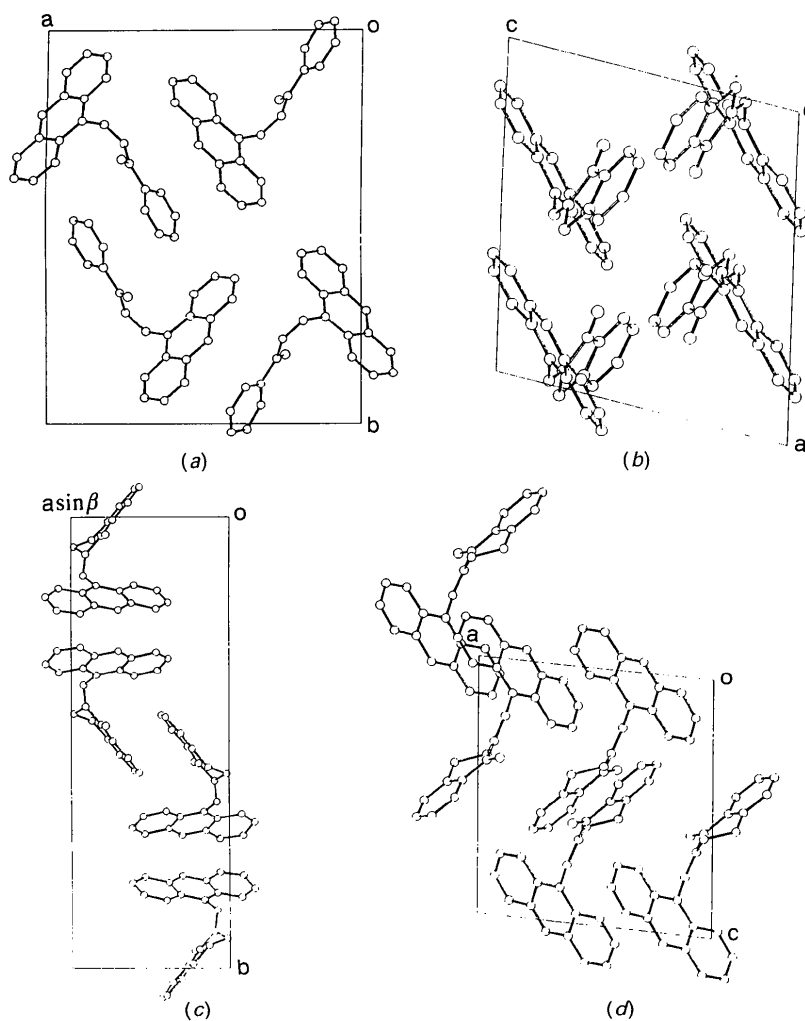

Fig. 2. Crystal structures: (a) cis-(I) viewed along the c axis; (b) cis-(III) viewed along the b axis; (c) cis-(IV) viewed along the b axis. The nearest neighbour of the original unit is also indicated (symmetry operation: −x, −y, 2 − z).

Fig. 2 shows the crystal structures. In *trans*-(IV) nearest neighbouring anthryl groups, which are related by a centre of symmetry, interact with van der Waals contacts. Although the distance between the least-squares planes is *ca* 3.4 Å, one anthryl group is significantly displaced with respect to the other along both the long and short axes of the anthracene, and as a result only a part of the anthracene moiety is involved in the π–π interaction. The close contacts are $C(1)\cdots C(13^i) = 3.604$ (5), $C(1)\cdots C(14^i) = 3.613$ (5), $C(2)\cdots C(11^i) = 3.616$ (5), $C(2)\cdots C(12^i) = 3.384$ (5), $C(2)\cdots C(13^i) = 3.227$ (5) and $C(3)\cdots C(13^i) = 3.663$ (5) Å ($i = -x, -y, 2 - z$). In *cis*-(I), *cis*-(III) and *cis*-(IV) there are no stacking interactions observed between the anthryl groups in the nearest neighbouring molecules. The crystal structures of the four compounds explain the lack of reactivity for [4 + 4] photodimerization of anthryl groups in the solid state.

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On the Crystal Structures of Two Inclusion Compounds of Tris(5-acetyl-3-thienyl)methane

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Abstract

The crystal structures of the ethanol and the ethyl acetate inclusion compounds of TATM, $CH(C_6H_5OS)_3$, were originally reported in space group $P1$, with two independent TATM molecules and one solvent molecule in the unit cell. However, the pairs of TATM molecules are closely related by centers of symmetry and the structures are better described in space group $P\bar{1}$. Refinements in $P\bar{1}$ led to lower e.s.d.'s and R values and to much more reasonable bond lengths, angles and U_{ij}'s for the TATM molecules; however, the solvent molecules are disordered and can be described no better in $P\bar{1}$ than they were in $P1$.

Introduction

Dillen, Roos and van Rooyen have now reported the crystal structures of four inclusion compounds of

tris(5-acetyl-3-thienyl)methane, TATM, in which solvent molecules are enclathrated within a framework of TATM host molecules. In the case of the *n*-hexane solvate, the ratio of TATM to solvent is 3:1 (Roos & Dillen, 1992); in the other three examples [benzene (van Rooyen & Roos, 1991*b*), ethyl acetate (van Rooyen & Roos, 1991*a*) and ethanol (Dillen & Roos, 1992)] the ratio is 2:1. In the latter two cases, ethyl acetate and ethanol, the structures were described in space group $P1$, with two molecules of TATM and one of solvent in the unit cell. However, in both cases the two TATM molecules are closely related by a center of symmetry and refinement in $P1$ led to improbable values for many bond lengths and angles, presumably due to the large correlations inherent in the refinement of a nearly centrosymmetric model in a noncentrosymmetric space group. Refinement in $P\bar{1}$, which requires the guest solvent molecules to be disordered, seems preferable, leading to improved R values and reasonable distances and