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Structure of a Cyclophane Host Molecule

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Abstract

The cyclophane tetramethyl 3,8,13,18a,21,26,31,36a-octahydro-4,6:9,12:22,24:27,30-tetraetheno-15,18,21:-33,36,39-diethenylylidenedibenzo[*k,a*1][1,8,17,24]-tetraoxacyclodotriacontene-1,2,19,20-tetracarboxyl-ate acetonitrile solvate, $C_{56}H_{44}O_{12}.CH_3C{\equiv}N$, contains a large cavity and forms host–guest complexes in solution with a variety of quaternary nitrogen compounds. Crystallization from an acetonitrile solution that contained adamantyltrimethylammonium iodide led, though, to crystals of the uncomplexed cyclophane (but containing one molecule of acetonitrile of crystallization). The cavity, about 7.6 × 4.0 Å and roughly rectangular in cross section, is occupied by ester groupings from two adjacent cyclophanes, entering from opposite sides. Crystal data: orthorhombic, $P2_12_12_1$, with $a = 11.741$ (6), $b = 16.155$ (5), $c = 25.895$ (7) Å, $V = 4912$ Å^3, $T = 296$ K, $Z = 4$, $M_r = 950.01$, $D_x = 1.28$ g cm^{-3}, $F(000) = 1992$, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.84$ cm^{-1}, $R = 0.0538$ for 2410 independent reflections with $I > 0$, $S = 2.29$ for 2610 total reflections.

Introduction

Cyclophane (I) and its tetracarboxylate derivative (II) (Fig. 1) have been studied extensively as hosts for a variety of guests. In water, the tetraanion (II) is a powerful receptor for a wide array of structures (Petti, Shepodd, Barrans & Dougherty, 1988). Most notable is the ability of (II) to tightly bind quater-

nary ammonium and imminium compounds through the 'cation–π' interaction. This novel binding force results from the positive charge of a guest being stabilized by direct contact with the electron-rich faces of the aromatic rings that form the walls of the receptor. Tetraester (I) serves as an efficient host for appropriate cation guests in organic media (Stauffer & Dougherty, 1988). These studies have led to a new model for the binding of the important neurotransmitter acetylcholine (Dougherty & Stauffer, 1990).

Cyclophanes (I) and (II) were designed to be fairly rigid structures with the six aromatic rings forming the walls of a central cavity. Modelling studies show
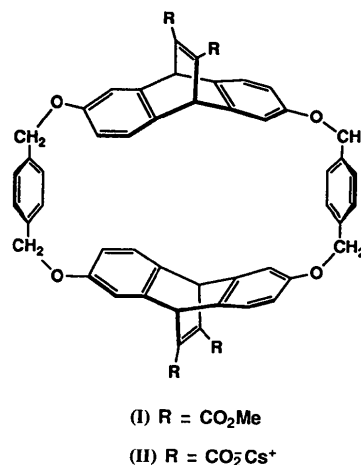

(I) R = CO₂Me

(II) R = CO₂⁻Cs⁺

Fig. 1. A schematic drawing of the cyclophane (I) and its tetra-carboxylate derivative (II).

that the molecule might adopt, in cross section, either a relatively rectangular or relatively circular shape. The esters/carboxylates were positioned to be well separated from the cavity, so as not to interfere with the guest–host interactions. While extensive NMR studies have supported this model, no direct structural data have been available.

We now report a structure for tetraester (I) that confirms the previous studies. Crystals were obtained from a solution that contained both (I) and ada-mantyltrimethylammonium (ATMA) iodide, an ideal guest for (I). However, crystals of (I) alone, plus an acetonitrile molecule of solvation, were obtained.

Experimental

The tetraester (I) was prepared as described by Petti *et al.* (1988), and was crystallized from an aceto-nitrile solution that also contained ATMA iodide (1:1 mole ratio) by a combination of vapor diffusion of water and evaporation of acetonitrile. After a preliminary photographic survey the crystal, a capped prism $0.22 \times 0.26 \times 0.59$ mm, coated with epoxy cement and covered with India ink to protect it from light, was mounted on an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation). The unit-cell dimensions and orientation matrix were obtained from the setting angles of 25 reflections having $20 < 2\theta < 26°$. Intensities were collected, by ω scans, for four octants (h, 0 to 11; k, -15 to 15; l, -24 to 24) to $2\theta = 40°$, at $4°$ min^{-1} over a range of $1.5°$; back-grounds were collected for 5 s at each scan extre-mum. The backgrounds measured for the very weak reflections were averaged in regions of 2θ and these averages were substituted for the measured back-grounds for *all* reflections, to increase precisions and reduce truncation losses (see *e.g.* Destro & Marsh, 1987). Three check reflections showed no significant variations.

There resulted 9882 intensities, which were aver-aged according to Laue symmetry *mmm* to yield 2610 independent observations; the goodness-of-fit for merging was 0.95, with variances σ_I^2 including, besides counting statistics, a term $0.014I^2$. An addi-tional lack-of-confidence term $0.014I^2$ was then added to the final variances σ_I^2. An E map calculated from the best *MULTAN* (Debaerdemaeker *et al.*, 1988) solution showed two small fragments (five and seven atoms) of the molecules; the remaining C, N and O atoms were recovered gradually from a series of structure-factor Fourier cycles. All H atoms were placed in assumed positions with C—H 0.95 Å (with the help of a difference section for the acetonitrile group) and were re-positioned once before the final least-squares cycles. Their parameters were not refined, but their contributions to F_c were included in the structure-factor calculations. Refinement was by least-squares minimization of $\Sigma w(F_o^2 - F_c^2)^2$ with weights w equal to the reciprocals of the variances $\sigma_{F^2}^2$. Initial convergence was reached at $R = 0.063$, $S = 2.7$; however, a difference map showed two peaks at about 0.5 e Å^{-3} in positions that strongly sug-gested alternative orientations of the two ester groups at C45 and C47. Eventually, three of the O atoms and one methyl group (O7, O8, O9, C46) were represented as disordered between two distinct sites, with a refinable population parameter; the remaining pair of atoms O10 and C48 seemed content in single sites, with their U_{ij}'s (and those of the central C atom C47) being able to compensate for the necessary disorder. The four atoms in the minor sites, with final population 0.16 (1), were refined as isotropic, and their H atoms were ignored; all other C, N and O atoms were anisotropic. The full-matrix cycles now involved 641 parameters [including a secondary-extinction coefficient; final value, 0.19 (4) × 10^{-6}]; at the end, the most significant shift was at 0.12σ, involving the minor site C46B. A final difference map had no feature as large as 0.3 e Å^{-3}. Final indicators: $S = 2.3$ for 2610 total reflections and 641 parameters; $R = 0.054$ for 2410 reflections with $I > 0.0$; $R = 0.050$ for 2293 reflections with $I > 3.0\sigma_I$. Incomplete modeling of the disorder can surely be blamed for at least some of the overruns.

Calculations were made on a VAX Station 3100 under the *CRYM* crystallographic computing system (Duchamp, 1964), using scattering factors from the *International Tables for X-ray Crystallography* (1974, Vol. IV); the secondary-extinction coefficient was that of Larson (1967; equation 3). Final coordinates are in Table 1;* they correspond to the chirality required by the synthesis (Petti *et al.*, 1988), which we did not attempt to confirm.

Discussion

A drawing of the molecule, including the numbering system, is shown in Fig. 2. The molecule has a roughly rectangular cross section, as predicted by Petti *et al.* (1988); there is a substantial cavity within the molecule, with an effective size of approximately 4.0×7.6 Å (Fig. 3). It had been our hope that the compound would crystallize with a portion of an ATMA molecule within the cavity; however, such co-crystallization did not take place. Neither was the acetonitrile molecule of solvation associated with the

A CYCLOPHANE HOST MOLECULE

Table 1. *Final heavy-atom parameters* (U_{eq} *in* Å²) *for* (*S,S,S,S*)-*host* (I)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	$U_{eq} \times 10^4$
O1	7798 (6)	41 (4)	2690 (3)	919 (25)
O2	6257 (5)	-344 (4)	2270 (3)	750 (21)
O3	7532 (6)	1559 (4)	3884 (3)	777 (21)
O4	7033 (5)	242 (4)	3737 (3)	816 (21)
O5	5895 (5)	3572 (4)	1288 (2)	694 (20)
O6	3486 (5)	5304 (4)	-961 (2)	744 (22)
O7	-2563 (9)	2610 (6)	-766 (3)	1498 (35)
O8	-2040 (7)	3002 (5)	-1514 (3)	1133 (28)
O9	-2927 (7)	4689 (5)	-1383 (3)	1159 (27)
O10	-2149 (6)	5790 (5)	-1042 (3)	984 (26)
O11	-955 (5)	3382 (3)	1449 (2)	617 (18)
O12	1481 (4)	1786 (3)	3764 (2)	507 (18)
C1	5616 (7)	2441 (5)	1824 (3)	446 (24)
C2	5853 (7)	3271 (6)	1783 (4)	494 (26)
C3	5997 (7)	3752 (5)	2229 (4)	502 (25)
C4	5925 (7)	3378 (6)	2708 (3)	482 (26)
C5	3391 (8)	1889 (5)	3529 (3)	405 (23)
C6	2311 (7)	1590 (5)	3402 (3)	417 (25)
C7	2121 (7)	1144 (5)	2954 (3)	438 (27)
C8	3042 (8)	986 (5)	2628 (3)	457 (25)
C9	5493 (7)	2029 (5)	3237 (3)	436 (23)
C10	5193 (7)	1190 (5)	2412 (3)	421 (23)
C11	6119 (6)	856 (5)	2766 (3)	427 (24)
C12	6258 (7)	1265 (5)	3203 (3)	427 (25)
C13	5529 (6)	2093 (5)	2303 (3)	384 (22)
C14	5703 (7)	2550 (5)	2749 (3)	379 (22)
C15	4277 (7)	1723 (5)	3196 (3)	363 (22)
C16	4113 (7)	1265 (5)	2744 (3)	370 (23)
C17	6830 (9)	141 (6)	2592 (4)	512 (29)
C18	6869 (8)	-1031 (6)	2047 (4)	919 (36)
C19	7025 (7)	1046 (7)	3635 (4)	544 (35)
C20	7770 (10)	-41 (8)	4162 (4)	1172 (40)
C21	5857 (8)	4437 (5)	1202 (4)	622 (27)
C22	5642 (7)	4594 (6)	640 (4)	532 (27)
C23	5798 (8)	3993 (6)	270 (4)	711 (30)
C24	5501 (8)	4126 (6)	-247 (4)	672 (30)
C25	5024 (8)	4866 (7)	-394 (4)	605 (30)
C26	4928 (9)	5478 (6)	-37 (5)	786 (34)
C27	5227 (9)	5337 (6)	479 (5)	789 (34)
C28	4639 (8)	4991 (6)	-945 (4)	746 (33)
C29	-738 (7)	3372 (5)	548 (4)	474 (24)
C30	-943 (7)	3831 (6)	996 (3)	469 (26)
C31	-1107 (7)	4660 (5)	969 (3)	467 (25)
C32	-1015 (7)	5074 (5)	503 (3)	455 (22)
C33	1579 (8)	5146 (5)	-735 (3)	522 (26)
C34	2625 (8)	4753 (7)	-828 (3)	569 (32)
C35	2727 (7)	3915 (6)	-808 (4)	583 (31)
C36	1778 (8)	3441 (5)	-685 (3)	548 (27)
C37	-530 (7)	4973 (5)	-470 (3)	446 (22)
C38	-366 (7)	3391 (5)	-430 (3)	455 (23)
C39	-1288 (7)	3708 (6)	-802 (3)	429 (25)
C40	-1353 (7)	4523 (6)	-825 (3)	453 (26)
C41	-648 (7)	3767 (5)	87 (3)	385 (24)
C42	-744 (7)	4630 (5)	64 (3)	393 (24)
C43	659 (7)	4659 (5)	-614 (3)	418 (25)
C44	741 (7)	3800 (5)	-589 (3)	443 (25)
C45	-2046 (10)	3086 (7)	-1049 (5)	867 (40)
C46	-2870 (15)	2409 (8)	-1735 (5)	1969 (65)
C47	-2172 (8)	5002 (7)	-1127 (4)	611 (34)
C48	-2946 (8)	6344 (6)	-1286 (4)	967 (39)
C49	-932 (7)	3835 (5)	1916 (4)	575 (25)
C50	-622 (7)	3287 (6)	2357 (3)	427 (24)
C51	-1076 (7)	2502 (6)	2392 (3)	560 (28)
C52	-780 (7)	1976 (5)	2799 (3)	545 (25)
C53	-17 (7)	2254 (5)	3169 (3)	438 (26)
C54	413 (7)	3040 (6)	3132 (3)	489 (25)
C55	129 (7)	3542 (5)	2721 (4)	460 (23)
C56	300 (7)	1694 (6)	3607 (3)	531 (28)
C57	2204 (14)	2428 (9)	4988 (5)	1486 (54)
C58	1019 (13)	2337 (8)	5175 (5)	952 (43)
N	192 (11)	2278 (9)	5332 (6)	1036 (44)

atoms in the walls (from O atoms involved in the ester linkage) range down to 3.28 (1) Å, and C⋯C distances (from the terminal methyl groups) down to 3.56 (1) Å. Although none of the ester groups penetrates completely into the center of the cavity, it is still perhaps best to think of the observed confor-
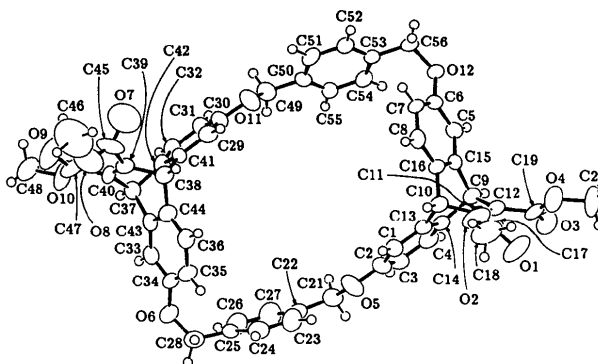

Fig. 2. An *ORTEP* (Johnson, 1965) view of (I), with the atom numbering. Heavy atoms are shown as their 50% probability ellipsoids and H atoms as spheres of arbitrary, small dimension. C11 is hidden behind O2.
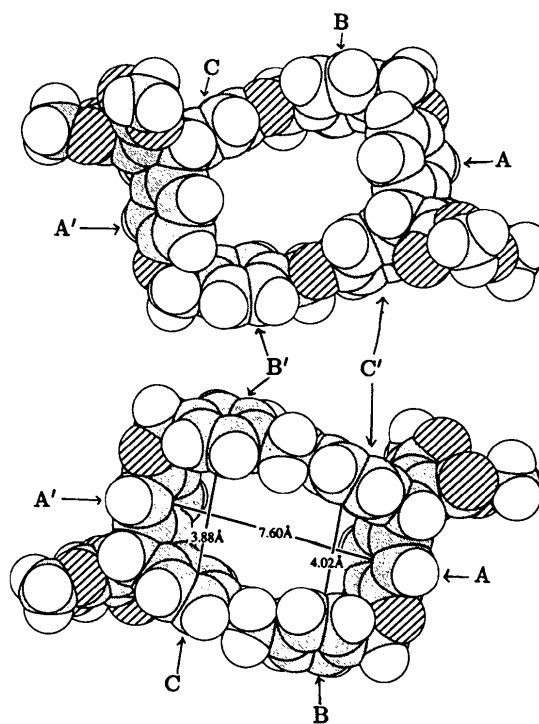

Fig. 3. Two views of (I) in space-filling representation, showing the dimensions of the cavity. The top view is the orientation of Fig. 2, and the bottom view is from the back - *i.e.* rotated by 180° about the horizontal axis. The six aromatic rings forming the 'walls' of the cavity are labeled *A–C*.

cavity; rather, the cavity is filled with ester groupings of two adjacent host molecules, one entering from either side. Two views of this arrangement are shown in Fig. 4. The guest ester groupings are packed quite snugly into the cavity: O⋯C distances to aromatic

mation of (I) as a binding conformation, rather than a conformation of free host. The shape of the cavity can be deduced from the distances across it given in Table 2. We note that the single ester grouping which enters the cavity from the right-hand side in Fig. 4(b) is disordered between two conformations; we show only the major orientation. The alternative orientation, with population 0.16 (1), is rotated by − 102° about the C—C bond; in this orientation, the terminal methyl group C46B lies outside the cavity.

Table 2. *Selected distances* (Å) *across the cavity in* (S,S,S,S)-*host* (I)

C1—C51	7.994 (12)	C27—C31	7.624 (13)
C1—C55	7.075 (12)	C8—C33	11.133 (12)
C2—C50	7.745 (12)	C8—C36	9.567 (12)
C3—C51	8.557 (12)	C5—C33	12.414 (12)
C3—C55	7.014 (12)	C5—C36	11.355 (12)
O5—O11	8.060 (8)	C6—C43	11.683 (12)
C21—C49	8.240 (12)	C6—C44	11.087 (12)
C23—C29	7.772 (13)	C7—C43	10.980 (12)
C23—C31	8.376 (13)	C7—C44	10.256 (12)
C27—C29	7.691 (14)		

Table 3. *Average bond distances* (Å) *for* (S,S,S,S)-*host* (I)

Bond type	Number of bonds	Average lengths*	Expected†
C—C(aromatic)	36	1.381 (16)	1.380 (13)
C(aromatic)—C(sp³)	4	1.500 (8)	1.510 (9)
C(sp³)—O(ether)	4	1.432 (20)	1.424 (12)
C(aromatic)—O(ether)	4	1.383 (9)	1.370 (11)
C(bridgehead)—C(aromatic)	8	1.524 (13)	1.515 (11)
C(bridgehead)—C(sp²)	4	1.527 (8)	1.510 (14)
C(sp²)—C(sp²)	2	1.320 (1)	1.317 (13)
C(sp²)—C(carbonyl)	4	1.480 (15)	1.488 (14)
C(carbonyl)—O(carbonyl)	4	1.206 (21)	1.196 (10)
C(carbonyl)—O(ester)	3‡	1.315 (19)	1.336 (14)
O(ester)—C(sp³)	4	1.459 (21)	1.448 (10)

* Quantities in parentheses are sample standard deviations.
† Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987).
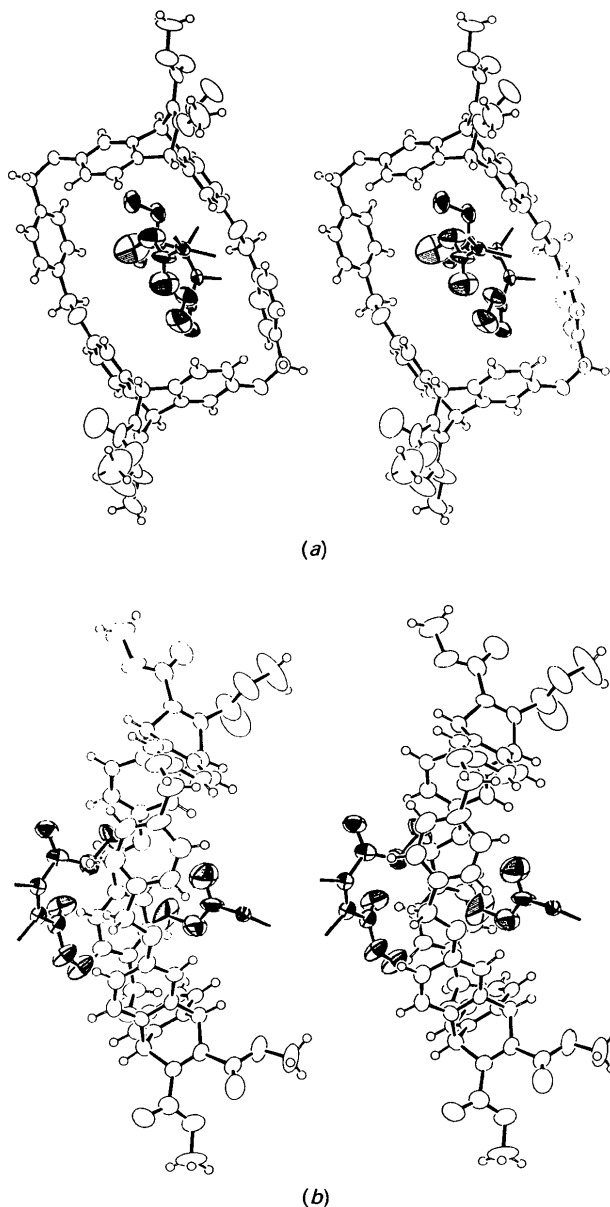‡ C45—O8, 1.212 (14) Å, not included.

(a)

(b)

Fig. 4. Stereoviews of (I), (a) perpendicular to the cavity and (b) 90° from (a) showing ester groupings of adjacent molecules entering from both sides of the cavity.

The cavity shows approximate twofold symmetry: disregarding the central p-xylylene groupings (rings B and B', Fig. 3), corresponding atoms in the two halves of the molecule map onto one another within 0.2 Å. Some atoms of rings B and B' show mismatches of about 0.5 Å, representing significantly different tilts of these rings relative to the central axis. The walls of the cavity are only approximately vertical. Rings C and C' are inclined (from the vertical) by about 10° and rings A and A' by about 30°; while ring B' is inclined by only 12°, ring B is inclined by 34°. Opposite walls are inclined in opposite directions, so that the two openings into the cavity have quite different shapes. In the present case, one side of the opening accommodates much of two methyl esters, while the other side accommodates but one.

Bond lengths and angles are, in general, normal, (Table 3) and we note only the following: the CH₂—O bond lengths between rings A and B, and between A' and B', are significantly longer [1.443 (6) versus 1.415 (6) Å] than those between B and C (and B', C'), reflecting the lack of conjugation due to the sharp bend in the molecule. The two adjacent bonds show similar but smaller effects, the differences bordering on insignificance.

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Studies on Photochromism of a Thermally Stable Fulgide in the Crystalline State: X-ray Crystallographic Investigation of (*E*)-2-Isopropylidene-3-(1-naphthylmethylene)succinic Anhydride

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Abstract

(*E*)-2-Isopropylidene-3-(1-naphthylmethylene)succinic anhydride, $C_{18}H_{14}O_3$, $M_r = 278.31$, monoclinic, $P2_1/c$, $a = 13.408$ (1), $b = 8.762$ (1), $c = 13.431$ (1) Å, $\beta = 117.50$ (1)°, $V = 1399.5$ (3) Å^3, $Z = 4$, $D_m = 1.32$, $D_x = 1.321$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.69$ mm^{-1}, $F(000) = 584$, $T = 298$ K, $R = 0.057$ for 1777 observed reflections. The electrocyclic ring closure that the title compound undergoes in the solid state is viewed in terms of relevant geometrical parameters. The photochromism of the compound observed in the solid state appears to occur at defect sites, surfaces and microcavities.

Introduction

Interest in studies on photochromic compounds has been increasing ever since the potential applications of photochromic materials were realised in various areas such as the control and measurement of radiation intensity, optical computers and display systems (Brown, 1971; Dürr, 1989; Dürr & Bouas-Laurent, 1990). Among the very useful, as well as widely investigated, classes of photochromic compounds are fulgides (Dürr & Bouas-Laurent, 1990; Hanazawa, Sumiya, Horikawa & Irie, 1992; Suzuki, Tomoda, Ishizuka, Kaneko, Furui & Matsushima, 1989; Zhao, Ming, Zhu & Fan, 1992). Detailed investigations of several aspects including the mechanism, thermal stability, reusability and potential applications of a

series of these compounds were carried out by Heller and co-workers (Heller & Megit, 1974; Hart, Heller, Megit & Szewczyk, 1975; Darcy, Heller, Strydom & Whittall, 1981; Heller & Langan, 1981; Heller, 1991). However, reports on the study of the mechanism of photochromism of these compounds in the solid state are relatively sparse. A report by Kaftory (1984) concerning the crystallographic study of a fulgide forms one example.

It was observed (Hart *et al.*, 1975) that irradiation of the yellow (*E*)-2-isopropylidene-3-(1-naphthylmethylene)succinic anhydride (I) at 366 nm in the crystalline state, in a rigid plastic matrix, and in benzene, produced a red coloration ($\lambda_{max} = 485$ nm) attributed to the formation of 4,4a-dihydrophenanthrene (DHP) (II). Upon exposure to white light, the colour change could be reversed, but did not occur in the dark. With the aim of gaining an insight into the structural aspects responsible for the observed phenomenon in the solid state, crystallographic analysis of the fulgide (I) has been carried out and the results are presented in this paper.

Yellow — (I) $h\nu_1$ (λ = 366 nm) / $h\nu_2$ (λ = 485 nm)   Red — (II)