ORGANIC COMPOUNDS

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Photoisomerization of Tetraethyl 6,8,15,17-Tetrahydro-7*H*,16*H*-5,18[1′,2′]-benzeno-9,14-ethenodibenzo[*a*,*h*]cyclotetradecene-7,7,16,16-tetracarboxylate. Structure of Tetraethyl 2,3,3a,7b,9,10,10a,14b-Hexahydro-1*H*,8*H*-3a,7b[1′,2′]-benzeno-10a,14b-ethenodibenzo[*a*,*e*]dicyclopenta-[*c*,*g*]cyclooctene-2,2,9,9-tetracarboxylate as its Methylene Chloride Solvate

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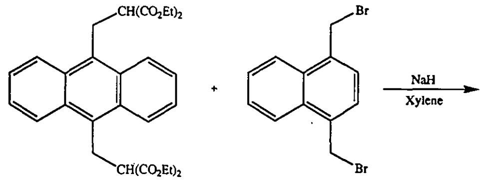
Abstract

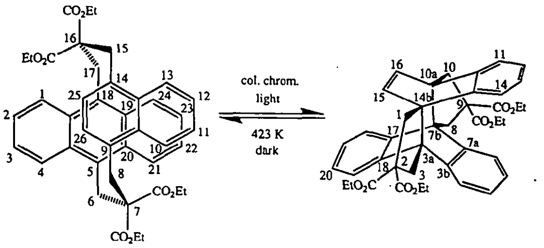
The initially formed cyclophane product, tetraethyl 6,8,15,17-tetrahydro-7*H*,16*H*-5,18[1′,2′]-benzeno-9,14-ethenodibenzo[*a*,*h*]cyclotetradecene-7,7,16,16-tetracarboxylate (I), produced from the cyclization of 9,10-bis{[2,2-di(ethoxycarbonyl)]ethyl}anthracene by treatment with sodium hydride followed by 1,4-bis(bromomethyl)naphthalene, was completely isomerized into its intramolecular [4πs + 4πs] cycloaddition product, tetraethyl 2,3,3a,7b,9,10,10a,14b-hexahydro-1*H*,8*H*-3a,7b[1′,2′]-benzeno-10a,14b-ethenodibenzo[*a*,*e*]dicyclopenta[*c*,*g*]cyclooctene-2,2,9,9-tetracarboxylate (II), when passed through a silica gel column under fluorescent light. The crystal structure analysis of (II) as its methylene chloride solvate showed that the length, 1.65 (1) Å, of each central bond, C3a—C14b and C7b—C10a, is larger than expected, and that the five-membered rings are exceptionally puckered.

Comment

Recently, compounds having photochromic properties have been studied intensely with regard to their applicability as reversible-image recording materials (Tazuke & Watanabe, 1982) and for solar-energy storage (Miki, Asako & Yoshida, 1987). Our interest in the temperature dependence of probe diffusion in various polymer matrices (Kim, Waldow, Han, Qui & Yamamoto, 1991) prompted us to prepare tetraethyl 6,8,15,17-tetrahydro-7*H*,16*H*-5,18[1′,2′]-benzeno-9,14-ethenodibenzo[*a*,*h*]-cyclotetradecene-7,7,16,16-tetracarboxylate (I) and its photoisomer, the intramolecular [4πs + 4πs] cycloaddition product tetraethyl 2,3,3a,7b,9,10,10a,14b-hexahydro-1*H*,8*H*-3a,7b[1′,2′]-benzeno-10a,14b-ethenodibenzo[*a*,*e*]-dicyclopenta[*c*,*g*]cyclooctene-2,2,9,9-tetracarboxylate (II), to verify their structures; that of (II) is given here.



(III) (IV)



(I) (II)

The tetraester 9,10-bis{[2,2-di(ethoxycarbonyl)]ethyl}anthracene (III) was prepared in 73% yield from the alkylation of diethyl malonate with 1.2 equivalents of NaH in THF followed by 0.5 equivalents of 9,10-bis(chloromethyl)anthracene under reflux for 24 h. Dibromide (IV) (Dixon, Fischer & Robinson, 1981) was made quantitatively by the bromination of 1,4-dimethylnaphthalene with 2.2 equivalents of *N*-bromosuccinimide and a catalytic amount of benzoyl peroxide in refluxing CCl_4 and benzene (2:1) (Antoun, 1987).

Our reaction leading to (I) and (II) was carried out with only minor changes from that reported by Shinmyozu, Inazu & Yoshino (1978) in that we allowed the dianion of (III) [prepared from the reaction of (III) with NaH] to react with (IV) in refluxing xylene in the dark. [We were un-

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† Fellow of the Alfred P. Sloan Foundation, 1991-1993.

able to detect the formation of (I) or (II) when the reaction was attempted with 1,4-bis(chloromethyl)naphthalene replacing (IV).] The ^{1}H NMR spectrum (400 MHz; $CDCl_3$) of the crude reaction mixture after aqueous work-up indicated a ratio of 1.2:1 of (I) (δ 5.60, *s*, 2H, C25 H and C26 H) to (II) (δ 6.30, *s*, 2H, C15 H and C16 H). The attempt to separate these products by flash-column chromatography (silica gel, 5% ethyl acetate in toluene) of the crude mixture under the laboratory fluorescent light gave only recovered (III) (18%), (II) (11% yield based on unrecovered starting material) and much polymeric material. Since (I) was no longer detected, it presumably cyclo-isomerized to (II) during the chromatography under the fluorescent laboratory lights. This assumption was supported by two observations. Heating (II) in anisole at 423 K for 5 h in the dark produced (I) in a mixture composed of (I) and (II) in a ratio of 3:2, based on ^{1}H NMR. After standing under laboratory fluorescent lights at room temperature, the solution in the same NMR tube was then re-examined and found to contain a substantially increased proportion of (II).

Shinmyozu, Inazu & Yoshino (1978) identified their product as (II) only on the basis of ^{1}H NMR spectral assignments. We became concerned with this assessment, however, because the NMR chemical shifts of the H atoms at C1, C3, C8 and C10, which we observed, are different from those reported by Shinmyozu, Inazu & Yoshino (1978). To verify the identity of (II) unequivocally, we determined its structure by X-ray analysis of the pale yellow prisms obtained by recrystallization from CH_2Cl_2. The crystals softened at about 383 K and completely melted at 423 K; Shinmyozu, Inazu & Yoshino (1978) reported m.p. 427-427.5 K. The X-ray analysis indicated the presence of a mole of CH_2Cl_2 per two moles of (II). The presence of CH_2Cl_2 was also exhibited in our ^{1}H NMR spectrum and may be responsible for our lower melting point. X-ray structures of related [$4\pi s + 4\pi s$]-photocyclized products, a naphthalenophane (Nishimura, Takeuchi, Takahashi & Sato, 1990) and an anthracene photodimer (Dougherty, Choi, Kaupp, Buda, Rudzinski & Osawa, 1986), have been reported recently.

The length of each central bond (C3a—C14b and C7b—C10a), 1.65 (1) Å, is slightly greater than the 1.631 Å reported for the anthracene photodimer (Dougherty, Choi, Kaupp, Buda, Rudzinski & Osawa, 1986). These unusually long central bonds (*cf.* 1.54 Å for $C_{sp^3}—C_{sp^3}$) may release some of the through-bond energy arising from the interaction among the three aromatic rings and the C15=C16 double bond (Dougherty, Choi, Kaupp, Buda, Rudzinski & Osawa, 1986). The geometries of the two five-membered rings are only slightly dissimilar and are somewhat distorted from those of typical five-membered rings (Vollhardt, 1987).

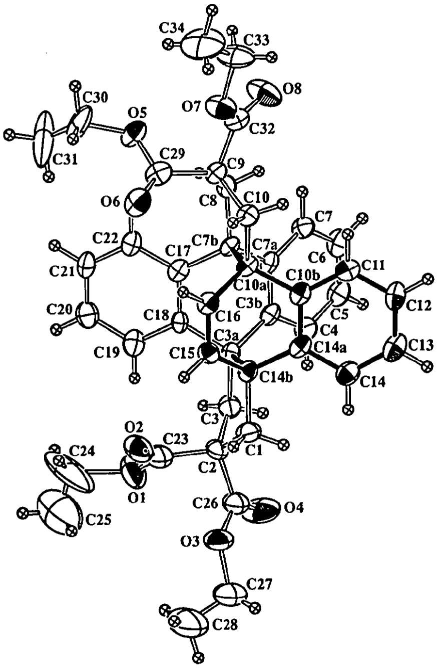

Fig. 1. Molecular configuration and atom-numbering scheme of (II) with displacement ellipsoids at the 30% probability level. H atoms are shown as unlabeled isotropic spheres of arbitrary radii. The CH_2Cl_2 molecule is not shown.

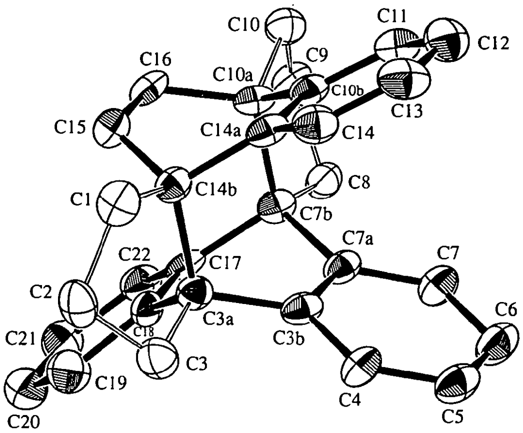

Fig. 2. The skeletal structure of (II) illustrating the various ring fusions.

Experimental

Compound (II)

Crystal data

$C_{42}H_{42}O_8.0.5CH_2Cl_2$
M_r = 717.26
Triclinic
$P\bar{1}$
a = 13.141 (3) Å
b = 14.219 (3) Å
c = 12.224 (3) Å
α = 113.60 (2)°
β = 109.71 (2)°
γ = 99.33 (2)°
V = 1849.7 (2) Å^3
Z = 2

D_x = 1.288 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 12.2-18.8°
μ = 0.153 mm^{-1}
T = 296 K
Equant
0.60 × 0.49 × 0.47 mm
Pale yellow

Data collection

Rigaku AFC-5S diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3643 measured reflections
3438 independent reflections
2011 observed reflections $[I > 3.0\sigma(I)]$

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 20°$
$h = 0 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 199 reflections intensity variation: 0.4%

Refinement

Refinement on F
$R = 0.067$
$wR = 0.077$
$S = 3.09$
2011 reflections
460 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.63$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	$U_{\rm eq}$
O1	1.0092 (7)	0.3724 (7)	0.5520 (8)	0.111 (3)
O2	0.9162 (6)	0.2000 (7)	0.4921 (8)	0.100 (3)
O3	1.0996 (6)	0.3635 (6)	0.8067 (7)	0.099 (3)
O4	1.0563 (6)	0.5142 (7)	0.8822 (8)	0.125 (3)
O5	0.2412 (5)	0.0247 (4)	0.0191 (6)	0.068 (2)
O6	0.3573 (6)	−0.0545 (5)	0.1022 (6)	0.077 (2)
O7	0.1159 (5)	−0.0774 (5)	0.1294 (6)	0.076 (2)
O8	0.1069 (6)	0.0891 (6)	0.2312 (7)	0.101 (3)
C1	0.8440 (8)	0.2717 (7)	0.6988 (8)	0.060 (3)
C2	0.9153 (8)	0.3529 (8)	0.6790 (9)	0.059 (3)
C3	0.8400 (8)	0.4212 (7)	0.6607 (8)	0.058 (3)
C3a	0.7137 (7)	0.3443 (6)	0.5748 (8)	0.042 (3)
C3b	0.6297 (8)	0.3993 (7)	0.6116 (8)	0.045 (3)
C4	0.6666 (7)	0.5026 (7)	0.7222 (8)	0.052 (3)
C5	0.590 (1)	0.5522 (7)	0.7484 (8)	0.058 (3)
C6	0.475 (1)	0.5021 (8)	0.668 (1)	0.064 (4)
C7	0.4361 (7)	0.3988 (7)	0.5564 (8)	0.050 (3)
C7a	0.5105 (8)	0.3464 (6)	0.5270 (8)	0.043 (3)
C7b	0.4698 (7)	0.2337 (6)	0.4034 (8)	0.041 (3)
C8	0.3414 (7)	0.1945 (6)	0.3076 (8)	0.047 (3)
C9	0.2878 (8)	0.0687 (6)	0.2410 (8)	0.045 (3)
C10	0.3521 (7)	0.0487 (6)	0.3559 (8)	0.050 (3)
C10a	0.4765 (7)	0.1357 (6)	0.4421 (8)	0.042 (3)
C10b	0.5175 (9)	0.1839 (6)	0.5933 (8)	0.044 (3)
C11	0.4444 (7)	0.1821 (7)	0.651 (1)	0.052 (3)
C12	0.485 (1)	0.2285 (8)	0.788 (1)	0.066 (4)
C13	0.601 (1)	0.2770 (8)	0.867 (1)	0.070 (4)
C14	0.6777 (8)	0.2816 (7)	0.813 (1)	0.058 (4)
C14a	0.6366 (8)	0.2351 (6)	0.6752 (9)	0.045 (3)
C14b	0.7154 (7)	0.2433 (6)	0.6095 (8)	0.043 (3)
C15	0.6721 (8)	0.1362 (7)	0.4852 (9)	0.049 (3)
C16	0.5604 (9)	0.0849 (6)	0.4063 (8)	0.047 (3)
C17	0.5497 (8)	0.2481 (6)	0.341 (1)	0.044 (3)
C18	0.6682 (8)	0.3042 (6)	0.4257 (8)	0.041 (3)
C19	0.7398 (8)	0.3269 (7)	0.370 (1)	0.063 (4)
C20	0.699 (1)	0.2930 (8)	0.235 (1)	0.067 (4)
C21	0.583 (1)	0.2346 (8)	0.1526 (9)	0.059 (4)
C22	0.5110 (8)	0.2147 (6)	0.205 (1)	0.051 (3)
C23	0.946 (1)	0.296 (1)	0.564 (1)	0.082 (5)
C24	1.031 (1)	0.328 (2)	0.419 (3)	0.27 (1)
C25	1.123 (2)	0.349 (2)	0.460 (2)	0.22 (1)
C26	1.031 (1)	0.422 (1)	0.803 (1)	0.08 (1)
C27	1.216 (1)	0.418 (1)	0.913 (1)	0.13 (1)
C28	1.292 (1)	0.408 (2)	0.867 (2)	0.26 (1)
C29	0.3037 (9)	0.0064 (7)	0.117 (1)	0.060 (4)
C30	0.232 (1)	−0.040 (1)	−0.114 (1)	0.11 (1)
C31	0.298 (2)	0.017 (1)	−0.148 (1)	0.21 (1)
C32	0.1600 (9)	0.031 (1)	0.201 (1)	0.063 (4)
C33	−0.008 (1)	−0.127 (1)	0.078 (1)	0.109 (4)
C34	−0.042 (1)	−0.236 (1)	−0.027 (1)	0.15 (1)
C35	0	0	1/2	0.31 (2)
Cl1†	0.1279 (8)	0.0902 (8)	0.607 (1)	0.197 (4)
Cl2†	−0.0915 (8)	−0.0318 (7)	0.527 (1)	0.174 (3)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.52 (1)	C7b—C17	1.53 (1)
C1—C14b	1.55 (1)	C8—C9	1.55 (1)
C2—C3	1.52 (1)	C9—C10	1.54 (1)
C3—C3a	1.54 (1)	C10—C10a	1.57 (1)
C3a—C3b	1.54 (1)	C10a—C10b	1.54 (1)
C3a—C14b	1.65 (1)	C10a—C16	1.50 (1)
C3a—C18	1.53 (1)	C14a—C14b	1.53 (1)
C7a—C7b	1.54 (1)	C14b—C15	1.49 (1)
C7b—C8	1.54 (1)	C15—C16	1.32 (1)
C7b—C10a	1.65 (1)		
C2—C1—C14b	108.3 (7)	C8—C9—C32	112.3 (8)
C1—C2—C3	101.8 (7)	C10—C9—C29	112.8 (7)
C1—C2—C23	112.3 (9)	C10—C9—C32	109.7 (7)
C1—C2—C26	110.4 (8)	C9—C10—C10a	108.6 (7)
C3—C2—C23	115.8 (8)	C7b—C10a—C10	105.0 (6)
C3—C2—C26	111.3 (9)	C7b—C10a—C10b	109.3 (6)
C2—C3—C3a	108.4 (7)	C7b—C10a—C16	111.0 (7)
C3—C3a—C3b	112.5 (7)	C10—C10a—C10b	113.8 (7)
C3—C3a—C14b	102.0 (6)	C10—C10a—C16	109.6 (7)
C3—C3a—C18	115.2 (7)	C10b—C10a—C16	108.2 (7)
C3b—C3a—C14b	111.6 (6)	C10a—C10b—C11	123.7 (9)
C3b—C3a—C18	103.5 (7)	C10a—C10b—C14a	117.1 (9)
C14b—C3a—C18	112.3 (6)	C10b—C14a—C14b	118.2 (8)
C3a—C3b—C4	122.8 (8)	C14—C14a—C14b	122.5 (9)
C3a—C3b—C7a	119.0 (8)	C1—C14b—C3a	104.1 (7)
C3b—C7a—C7b	118.3 (8)	C1—C14b—C14a	114.4 (7)
C7—C7a—C7b	122.9 (8)	C1—C14b—C15	110.2 (7)
C7a—C7b—C8	112.9 (7)	C3a—C14b—C14a	110.1 (6)
C7a—C7b—C10a	112.3 (6)	C3a—C14b—C15	110.9 (7)
C7a—C7b—C17	104.5 (7)	C14a—C14b—C15	107.3 (7)
C8—C7b—C10a	102.4 (6)	C14b—C15—C16	120.8 (8)
C8—C7b—C17	113.4 (7)	C10a—C16—C15	119.4 (8)
C10a—C7b—C17	111.7 (6)	C7b—C17—C18	118.0 (8)
C7b—C8—C9	110.3 (7)	C7b—C17—C22	123.6 (9)
C8—C9—C10	101.2 (6)	C3a—C18—C17	119.9 (8)
C8—C9—C29	113.9 (7)	C3a—C18—C19	122.0 (9)

Initial attempts at data collection were unsatisfactory because of crystal decay. To avoid the decay problem, this data set was collected at relatively high speed [12° min^{-1} (in ω)] with no rescans of weak reflections.

There is a single partially disordered methylene chloride molecule in the unit cell. Its presence was confirmed by ^{1}H NMR. The C atom of the group resides on a center of symmetry and the site is fully occupied. The two attached Cl atomic sites in the asymmetric unit have occupancy values of 0.5. However, the symmetry center generates two additional half-occupied Cl sites in the second asymmetric unit, completing the molecule on a statistical basis. The two H atoms of the methylene chloride group (which must also be disordered) were not included in the model.

During the final stages of refinement the H atoms were placed at assumed positions (C—H = 0.95 Å, $U = 1.2 \times U_{\rm eq}$ of the parent C atom) and fixed. The combination of undesirable data collection conditions and modeling errors, resulting from the disordered methylene chloride group, inevitably led to a less than exemplary refinement.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*, *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*R*)-(+)-2-Phenylpropyl *p*-Toluenesulfonate, $C_{16}H_{18}O_3S$

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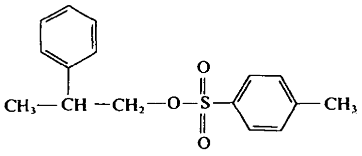
Abstract

The structure of an important precursor of a ferroelectric liquid crystal is reported. The two phenyl rings are nearly coplanar, having a dihedral angle of 5.0°, and are at a distance of 3.79 (2) Å from each other.

Comment

In connection with a project on the design and synthesis of ferroelectric liquid crystals (FLC), we required an efficient route to obtain several chiral precursors (Merlo, Gallardo, Taylor & Kroin, 1993). (*S*)-(−)-Ethyl lactate is particularly attractive as a chiral synthon as it is readily available in both enantiomeric forms with very high optical purity and, therefore, has been used in numerous applications (Seuring & Seebach, 1977). Recently, we described an efficient method for the preparation of (*R*)-(−)-*p*-(2-methylhexyl)aniline, (1), from (*S*)-(−)-ethyl lactate (Merlo & Gallardo, 1993), which is of considerable interest as a building block for liquid-crystalline materials having ferroelectric properties.

We have also found that the optical purity of the aniline enantiomeric to (1) can be ensured by using (*R*)-(+)-2-phenylpropyl *p*-toluenesulfonate (2) as a crystalline intermediate (Merlo & Gallardo, 1993). The molecular structure determination of the title compound (2) was undertaken by X-ray diffraction. The stereochemistry of



(2)