

Extended systems of closed helicene. Synthesis and characterization of [7] and [7.7]-circulene

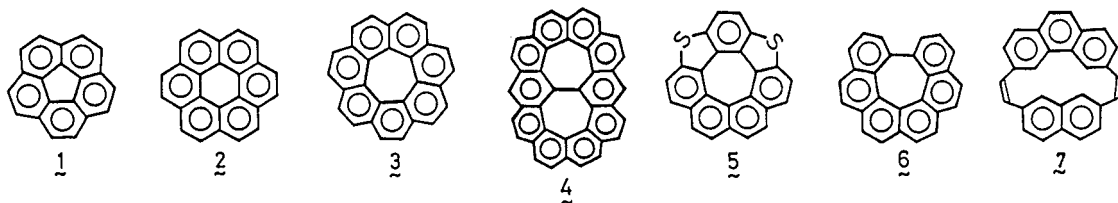
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Abstract - The polycyclic aromatic compounds with a circular arrangement of seven benzene rings, [7]circulene, was prepared, and its unusual saddle-shaped structure with C_2 symmetry was supported by its X-ray analysis. Preparation and characterization of [7.7]-circulene with unique 8-shaped and saddle-shaped geometry was also reported.

INTRODUCTION

Recent advances in large carbon cluster chemistry (fullerenes) where curved molecular surfaces on sp^2 carbon lattices have aroused a large interest in the field of polycyclic aromatic compounds with circular arrangement of benzene rings known as closed helicene; namely, circulene.¹⁻³

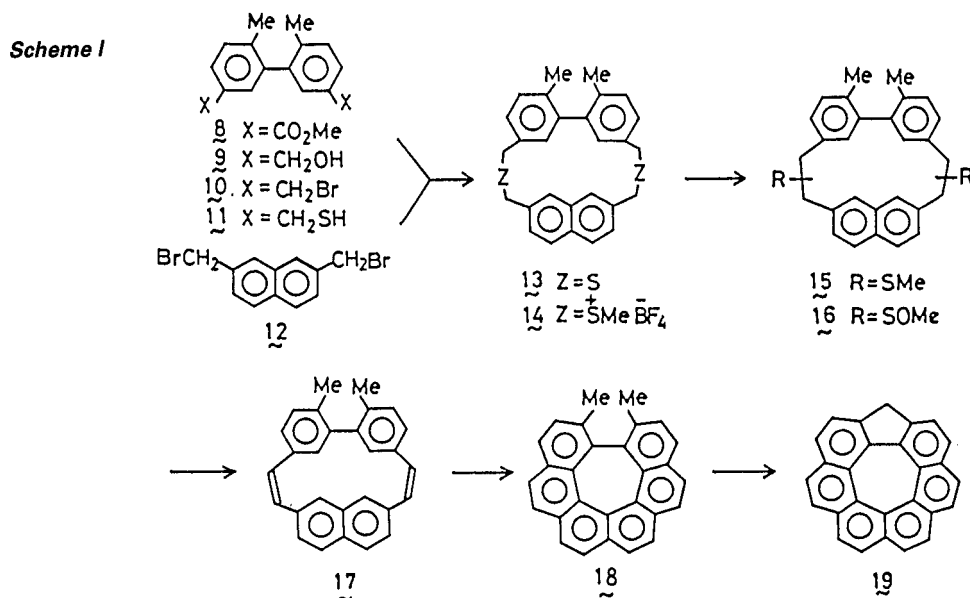


Within the family of circulene, there have been prepared [5]circulene (corannulene)^{4,5} (1) and [6]circulene (coronene) (2).⁶ Conspicuous features in circulene molecules are the existence of three types of geometry, bowl shaped nonplanar, planar, and saddle-shaped nonplanar, each resulting from the number of benzene rings necessary to form the circular arrangement. [5]Circulene (1) (C_{5v} symmetry), first reported and studied by Barth and Lawton in 1966, was shown to have a bowl-like shaped geometry by X-ray analysis.⁷ On the other hand, [6]circulene (2) (D_{6h} symmetry) is a well-known member of the class prepared by Scholl and Mayer in 1932 and has a completely planar structure because of the angular fusion of six benzene rings.⁸ [7]Circulene (3), the next higher homologue of [6]circulene (2), has been of interest for many years because of its anticipated strained and unique saddle-shaped molecular shape with C_2 symmetry as expected from the examination of its molecular model. Although the related compounds of [7]circulene (3) such as [7]heterocirculene (5)³ (incorporating thiophene rings) and hexa[7]circulene (6)⁹ (contiguous benzoannulated ring around a central seven-membered ring) have been recorded, the parent carbocyclic structure, [7]circulene (3), was still an unknown compound, in spite of an enormous amount of effort in its preparation.^{3,10}

We have been interested in the synthetic studies of twisted π -electron systems,¹¹ and previous papers described the syntheses of various strained cyclophanes with twisted aromatic rings.¹² An obvious extension of our interests in these studies led us to investigate the preparation of highly symmetrical and highly strained polycyclic aromatic molecules, [7]circulene (**3**) and [7.7]circulene (**4**), as one of a series of our synthetic studies of strained aromatic molecules.^{13,14}

RESULTS AND DISCUSSION

We reasoned that Reiss's attempted photocyclization¹⁰ of the cyclophane intermediate **7** directly into [7]circulene (**3**) failed because of the inherent rigid structure of **7**, incorporating both naphthalene and phenanthrene moieties. Thus, we directed our efforts to a two-stage synthetic approach that involves (1) photocyclization of the more flexible biphenylnaphthalene cyclophanes **17** and **29** and (2) modification of the chains to secure the missing benzene ring to complete the synthesis.

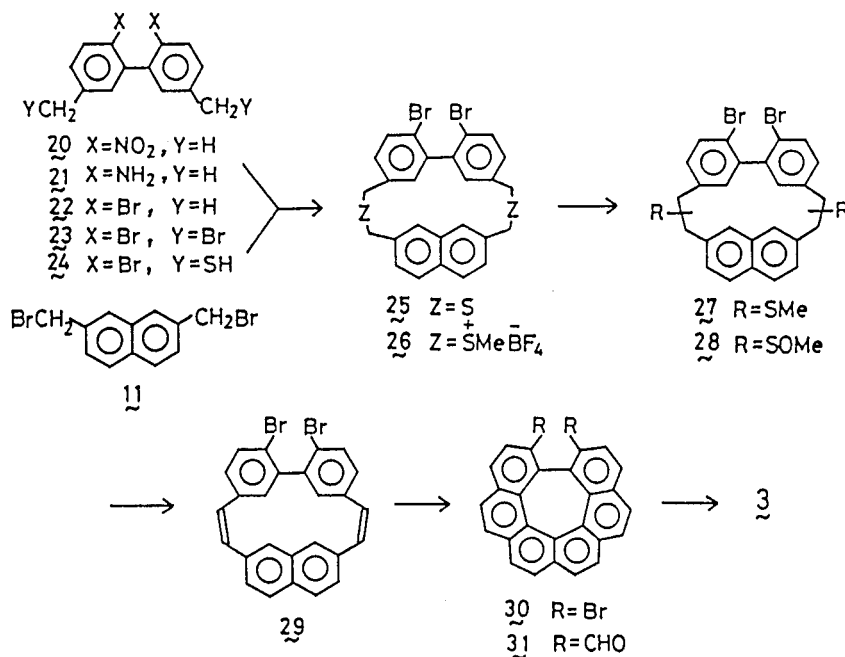


Synthesis of [7]circulene (3**):** First, we carried out an attempted preparation of [7]circulene (**3**) from 1,16-dehydro-2,15-dimethylhexahelicene precursor (**18**) to complete the synthesis according to the Reiss procedure (Scheme I). Lithium aluminum hydride reduction of 5,5'-dicarbomethoxy-2,2'-dimethylbiphenyl (**8**)¹⁵ afforded the alcohol **9** which was converted to the bisbromomethyl derivative **10** with phosphorus tribromide, and this was then submitted to the thiourea method under the usual reaction conditions to afford the bis(mercaptomethyl)biphenyl **11**. The coupling of dithiol **11** and 2,7-bis(bromomethyl)naphthalene (**12**)¹⁶ was carried out in *N,N*-dimethylformamide with cesium carbonate to give the dithiacyclophane **13**, mp 143-144 °C (54% yield). Reaction of cyclophane **13** with dimethoxycarbonium fluoroborate in dichloromethane yielded the disulfonium salt **14** whose Stevens rearrangement mediated by sodium hydride provided a 93% yield of the bis(sulfide) **15** as an oil. Oxidation of **15** with *m*-chloroperbenzoic acid gave the bis(sulfoxide) **16** whose pyrolysis at 300 °C (0.001 mm) produced the unsaturated cyclophane **17**, as pale orange needles, mp 145-146 °C (45% yield from **15**). A solution of cyclophane **17** containing a trace amount of iodine was irradiated with a high-pressure mercury-quartz lamp¹⁷ in a photolysis tube through which a slow and fine stream of nitrogen was passed. Through monitoring the reaction by UV absorption spectra, it was determined that a 2-h irradiation was enough to afford a

maximum yield of 1,16-dehydro-2,15-dimethylhexahelicene (**18**) (57% yield), mp 226-228 °C, pale yellow prisms. Its ^1H NMR spectrum showed the expected absorption peaks: a singlet at δ 1.75 for two methyl protons and a multiplet at δ 7.0-7.9 for twelve aromatic protons. Comparison of the UV absorption spectrum of **18** (λ_{max} 245, 269, 275, 282, 308, 325 nm) with that of 1,16-dehydrohexahelicene (**6**)⁹ also supports this structure.

An attempt to halogenate the two methyl positions of **18** by use of either NBS or NCS was unsuccessful, invariably giving a polymer as the product. Several other attempts were made to synthesize [7]circulene (**3**). Dehydrogenation of **18** with 5% Pd/C and Pd-S/BaCO₃ at 320-330 °C was observed to afford the [7]circulene analogue **19** incorporating a cyclopentadiene unit within the framework (51-65% yield), mp > 300 °C, as yellow plates. The ^1H NMR spectrum revealed that two methyl groups had been lost and showed a new peak at δ 3.99 (2H, singlet), while the aromatic resonance multiplet resembled that of the starting dimethyl compound **18**. This evidence, enhanced by its mass spectrum and its suitable elemental analysis, pointed to 1,16-dehydro-2,15-methano-hexahelicene (**19**) as the product, which seems to be a nearly planar molecule by examination of its molecular model.

Scheme II

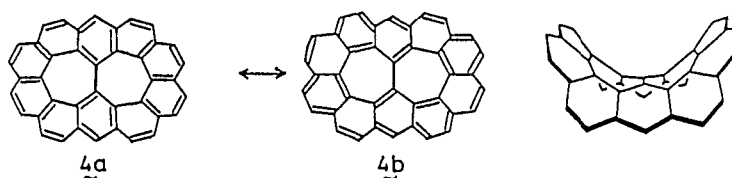


In the next approach, we selected as the key intermediate 1,16-dehydro-2,15-dibromohexahelicene (**30**) (see Scheme II) which was easily convertible into the precursor **31** with a suitable substituent for ring closure to give the final benzene ring. 2,2'-Diamino-5,5'-dimethylbiphenyl (**21**), provided by the reduction of 5,5'-dimethyl-2,2'-dinitrobiphenyl (**20**)¹⁸ with tin and concentrated hydrochloric acid, was treated with sodium nitrite to afford the corresponding diazonium salt whose mercuric bromide complex¹⁹ was pyrolyzed at 110 °C to give the 2,2'-dibromo-5,5'-dimethylbiphenyl (**22**), mp 109-110 °C (40% yield from **20**). N-Bromosuccinimide bromination of **22** afforded the bis(bromomethyl)derivative **23**, which was converted into the bis(mercaptomethyl)-biphenyl **24** by a routine procedure (48% yield from **22**). The coupling reaction of **24** and **12** was carried out following the procedure described for the preparation of **13**, and column chromatography of the reaction product afforded the dithiacyclophane **25** in 56% yield, mp 173-174 °C. The dithiacyclophane **25** was converted into the disulfonium salt **26** whose Stevens rearrangement gave a 95% yield of bis(sulfide) **27** as an oil. Oxidation of **27** with m-chloroperbenzoic acid followed by

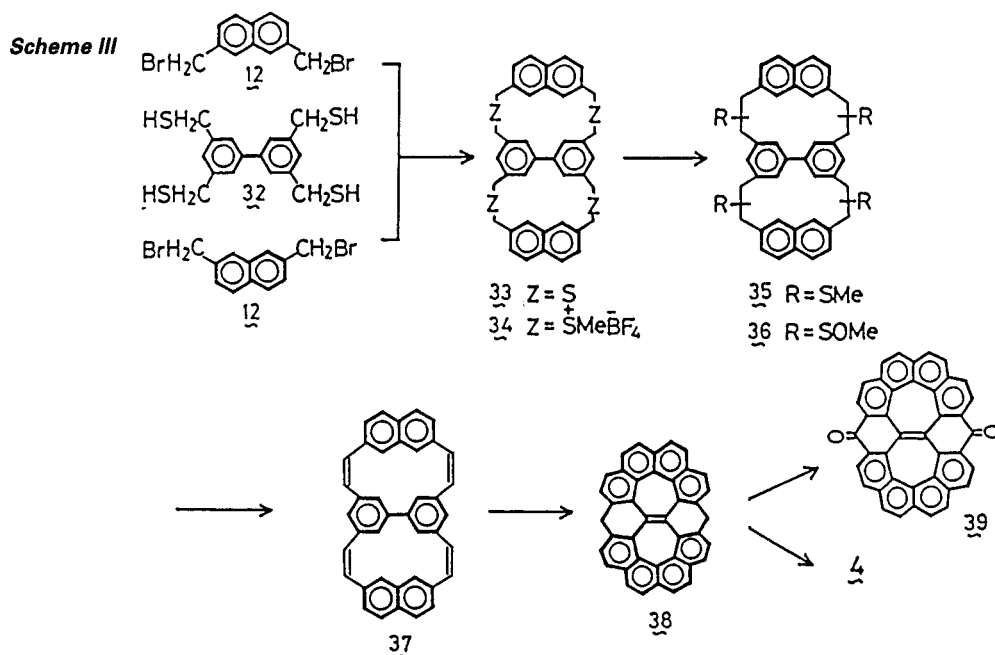
pyrolysis (300 °C, 0.001 mm) produced a 63% yield of the cyclophanediene **29**, mp 213-214 °C. Photocyclization of the diene **29** under a similar condition described for the preparation of **18** led to the formation of 1,16-dehydro-2,15-dibromohexahelicene (**30**), mp 299-301 °C, in 47% yield. Its ¹H NMR spectrum showed the expected absorption at δ 7.82-8.66 (multiplet). UV and MASS spectroscopy confirmed the structure **30**. Lithiation of the dibromide **30** with n-BuLi in tetrahydrofuran and formylation of the resulting dilithio derivative of **30** with dimethylformamide gave, as was expected, the dialdehyde **31** (35% yield, 303-305 °C) and 1,16-dehydrohexahelicene (**6**) (4% yield, mp 163-164 °C) as the reductive product of dibromide **30**.

For the introduction of the final benzene ring into circular arrangement, we found that reductive coupling of the dialdehyde **31** with low-valent titanium effected a clean-coupling reaction to produced [7]circulene (**3**). Intramolecular reductive coupling of **31** with LiAlH₄ and titanium trichloride in dimethoxyethane completed the outer perimeter and afforded a 35% yield of [7]circulene (**3**) as yellow plate, mp 295-296 °C (from benzene-hexane). The ¹H NMR is characteristic having a single sharp peak at δ 7.45, and the ¹³C NMR exhibiting three peaks at δ 136.0, 131.1, and 127.5 corresponds to the molecular symmetry. The mass spectrum showed only significant ions at M⁺, M⁺+1, and M⁺+2. The UV spectrum of **3** showed absorption maxima (nm) at 236 sh (log ε 4.44), 266 sh (4.86), 275 (5.14), 296 (4.46), 331 (3.91), 383 sh (2.90), and 4.03 (2.83). The remarkable hypsochromic shift (27 nm) with decreasing extinction coefficient of the highest absorption going from the [6]circulene (**2**) to the [7]circulene (**3**) indicates a nonplanar saddle-shaped geometry which is confirmed by its X-ray analysis shown below.

Synthesis of [7.7]circulene (4). An obvious extension of our interests in these studies directed our efforts to the preparation of the unique 8-shaped and saddle-shaped [7.7]circulene (**4**)²¹ with contiguous benzoannulated rings around a central bicyclo[5.5.0]dodecane framework. This molecule consists of ten benzene rings and has a total of forty π electrons. However, the canonical structure **4b** suggests that the molecule might behave as a heptalene²² with a 28 π-electron periphery. The canonical form **4b** is unique for it can in principle, be converted into an aromatic system by the addition or removal of electrons. The consideration of these structural factors led us to synthesize the novel 8-shaped [7.7]circulene (**4**) (see Scheme III) which has revealed the strained nonplanar and unusual saddle-shaped geometry anticipated from the examination of its molecular model.



The termolecular coupling of the tetrathiol **32**²³ and two equivalents of 2,7-bis(bromo-methyl)naphthalene (**12**) was carried out in dimethylformamide with cesium carbonate to give the tetrathiacyclophane **33** (mp > 300 °C, 40% yield). Reaction of **33** with dimethoxycarbonium tetrafluoroborate in dichloromethane yielded the tetrasulfonium salt **34**. Subsequent Stevens rearrangement mediated by sodium hydride provided a 21% yield of the tetrasulfide **35** as a yellow oil. Oxidation of **35** with m-chloroperbenzoic acid gave the tetrasulfoxide **36** whose pyrolysis at 300 °C (0.001 mm) produced the unsaturated cyclophane **37** (yellow prisms, mp 176-178 °C, 16% yield from **35**). A cyclohexane solution of **37** containing a trace amount of iodine was irradiated using a high-pressure mercury lamp for 2 h to afford the dihydro[7.7]circulene (**38**) (yellow



prisms, mp > 350 °C, 12% yield), which was isolated by chromatography on silica. The ¹H NMR (CDCl₃) revealed that two methylene groups showed an AB quartet at δ 4.50 (4H) and two sets of AB quartet aromatic resonances at δ 7.53(8H) and 7.56(8H). This evidence, supported by its mass spectrum and its correct elemental analysis, pointed to dihydro[7.7]circulene (**38**) as the product, which seems to be a saddle-shaped nonplanar molecule. The existence of two methylene groups of **38** was also confirmed by its oxidation with selenium oxide in dioxane which gave the novel quinonoid derivative **39** in 21% yield (as well as 14% of the monoketone, mp 210-212 °C) stable orange prisms (from benzene), mp > 300 °C.

For the introduction of the final two benzene rings into the circular arrangement, we found that dehydrogenation of **38** with triphenylmethyl perchlorate in acetic acid afforded a 25% of [7.7]circulene (**4**), stable pale orange prisms, mp > 300 °C (from benzene). The NMR data are characteristic: the ¹H NMR spectrum has a single peak at δ 7.61 and two set of AB systems (δ_a 7.45, δ_b 7.47, J_{ab}=6.22Hz, 8H; δ_a 7.47, δ_b 7.56, J_{ab}=7.72Hz, 8H), the ¹³C NMR spectrum exhibits twelve peaks at δ 126.4, 126.8, 127.2, 131.2, 131.7, 132.3, 132.8, 136.6, 136.4, 136.9, and 137.3 corresponds to the molecular symmetry. The UV spectrum showed absorption maxima (nm) at 274 (log ε 5.09), 301 (4.75), 316 (3.94), 362 (4.01), 415 (3.75), and 440 (3.51). These spectral properties of **4** and its thermal stability indicate that this molecule is best represented by the structure **4a** consisting of two hexa[7]circulene units.

Syntheses and Chiroptical Properties of Optically Active 1,16-Dehydrohexahelicene Derivatives 6, 18, 30, and 31. 1,16-Dehydrohexahelicene (hexa[7]circulene) (**6**) with C₂ symmetry was predicted, on the basis of the molecular model, to be saddle-shaped and potentially resolvable.²⁴ While the hydrocarbon **6** has been synthesized, no evidence concerning its chiral properties has yet appeared.⁹ Our continuing interest in chiroptical properties of chiral π-electron systems¹¹ has led us to investigate the preparation and absolute configuration of optically active compounds **6**, **18**, **30**, and **31** as well as their optical stabilities.

1,16-Dehydrohexahelicene (**6**) itself was resolvable at low temperature by chromatographic resolution²⁵ by using a column packed with (+)-poly(triphenylmethyl methacrylate)²⁶ (elution with methanol) but extremely optically labile (half-life, 10 s, at -5 °C) (ΔG[‡] 17 Kcal/mol). However, other compounds (**18**, **30**, and **31**) of this type

with 2,15-disubstituents could be resolved by the chromatographic method to give optically pure (-)-(M)-**18**, (+)-(P)-**18**, (-)-(M)-**30**, (+)-(P)-**30**, (-)-(M)-**31**, and (+)-(P)-**31**, with $[\alpha]_D$ (CHCl₃) -1882°, +1879°, -2110°, +2113°, -1456°, and +1450°, respectively. Comparison of their CD spectra with that of authentic (-)-(M)-hexahelicene established their absolute configuration.

Thermal racemization of their enantiomers (**18**, **30**, and **31**) monitored by polarimetry was found to have moderate optical stability, the half-life of racemization being 120 min (at 139 °C in xylene) for the dimethyl derivative (**18**) (ΔG^\ddagger 32 Kcal/mol), 220 min for the dibromide (**30**) (ΔG^\ddagger 33 Kcal/mol), and 100 min for the dialdehyde (**31**) (ΔG^\ddagger 32 Kcal/mol). The capacity of the 2,15-substituents to interfere with passage through the planar transition state thus seems to be Br > CH₃ > CHO >> H. It might be noted that this order roughly parallels the order of size of the groups.

Molecular Structures of [7]Circulene (3) and 1,16-Dehydro-2,15-dibromohexahelicene (30). The molecular structure of [7]circulene (**3**) was determined by the single-crystal X-ray diffraction method at room temperature (at 20 °C). In order to obtain structural parameters with higher accuracy, redeterminations of the crystal structure of **3** was carried out at low temperature (at -110 °C). The two different views of the molecular structure of **3** are shown in Figure 1. As expected, the molecule **3** has the unique saddle-shaped structure (Figure 1a). The molecule **3** has a crystallographic two-fold symmetry passing through the C(2) and C(1) atoms and the midpoints of C(12)-C(12') and C(15)-C(15') bonds (Figure 1b). The central seven-membered ring is described as the boat form with the base plane defined by C(1), C(14'), C(12), and C(13) atoms, with C(14) atom as the bow and with C(12') and C(13') atoms as the stern, or its symmetry equivalent structure related by the twofold axis. The dihedral angles between the base plane and the bow or stern planes are 21.7° and 26.5°, respectively.

The molecular structure of 1,16-dehydro-2,15-dibromohexahelicene (**30**) determined by the X-ray diffraction method is shown in Figure 2 together with the atomic numberings. The molecule has an approximate twofold symmetry axis that coincides with the C(10)-C(23) bond and the midpoint of the C(20)-C(26) bond. The molecule **30** is also described as a saddle-shaped structure (Figure 2a) of molecule **3**; however, the deformation of the former is relatively large compared with the rather flat structure of **3**. The seven-membered ring in the center of the molecule is the boat form with the base plane defined by C(20), C(21), C(23), and C(24) atoms, with C(22) atom as the bow and with C(25) and C(26) atoms as the stern, or its alternative one related by noncrystallographic twofold symmetry. The dihedral angles between the base plane and the bow or stern planes are 17.7° and 36.4°, respectively.

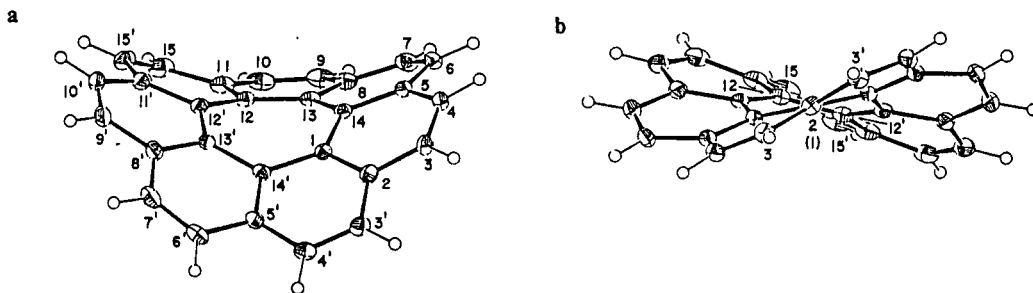


Figure 1. Molecular structure of **3** determined at -110 °C. Thermal ellipsoids for non-hydrogen atoms are drawn at 30% probability level. The hydrogen atoms are shown as the spheres with arbitrary temperature factor of 1.0 Å²: (a) a view showing saddle-shaped structure and (b) a molecular projection along the crystallographic two-fold axis.

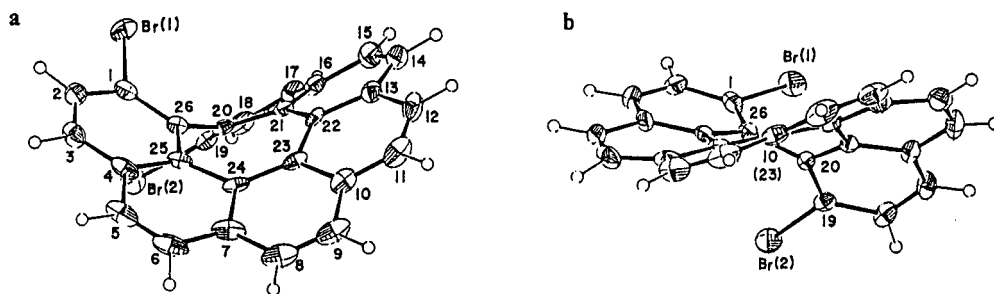


Figure 2. Molecular structure of 30. Drawing conditions are the same as those in Figure 1: (a) a view showing the saddle-shaped structure and (b) a molecular projection along the noncrystallographic two-fold axis.

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