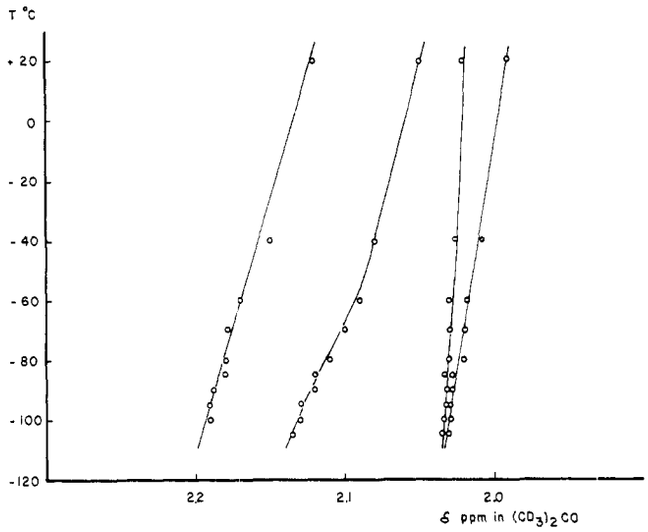

Figure 4. Changes in chemical shifts of acetoxyl group signals of 1 in acetone-d_6 over the temperature range +20 to −105 °C, determined from 250-MHz spectra.

crystallized, there are related instances, for example D-ribose diethyl (and diphenyl) dithioacetals[1] and their tetraacetates,[9] for which NMR studies in solution at room temperature indicate population by mixtures of conformers,[1] whereas comparative X-ray crystallographic studies[11] have revealed a single conformer present in the same compound in the crystalline state.

For molecules that display evidence of conformational flexibility, it is thus understandable, and maybe to be expected, that the conformation adopted in the solid state will correspond most closely to that present in solution at low temperature and will not necessarily be one that is preponderant at room temperature. The present example provides a particularly favorable molecule for observing this conformational mobility over a wide temperature range. This type of experiment would not be feasible for most water-soluble acyclic carbohydrates and their derivatives because of strong conformational bias, poor spectral resolution, and the limited temperature range available with suitable solvents in the liquid state.

Experimental Section

NMR Spectra. Spectra were recorded at 250 MHz with a CAMECA-250 spectrometer (Thomson CSF, Paris) with solutions (~13%) of 1 in acetone-d_6 containing ~5% of tetramethylsilane as internal reference (δ 0.00) and lock signal. At each of the temperatures indicated, the spectrum was recorded initially at 3000-Hz sweep width; detailed examination of the spectrum was then performed at 300-Hz sweep width for measurement of exact chemical shifts and line spacings. Values were recorded as indicated at progressively lower temperatures, allowing time for thermal equilibration at each temperature; some line broadening occurred at the lower temperatures and the signals collapsed abruptly into featureless broad humps at −120 °C as the solution froze. Spectra were again recorded at selected temperatures as the temperature was raised progressively to +20 °C; no significant differences were observed at corresponding temperatures with spectra recorded at successively lower temperatures. Temperature calibration was achieved by reference to signals of *o*-dichlorobenzene for temperatures >0 °C and by use of isopentane for temperatures <0 °C; a thermocouple was inserted directly in the sample tube. The temperatures indicated are considered correct to ±2 °C.

The experiments were repeated with 2-chloro-1-propene-d_5 as the solvent; the results were essentially similar to those recorded for solutions in acetone-d_6 except for minor differences in chemical shifts and spin coupling values; the solution froze at approximately −140 °C.

Tetra-*O*-acetyl-D-ribose Diisobutyl Dithioacetal (1). A solution of D-ribose diisobutyl dithioacetal[10] (6 g) in pyridine (18 mL) and acetic anhydride (24 mL) was kept for 18 h at ~20 °C and then poured into water. The product (1) was then isolated by conventional extraction with chloroform and obtained as an oil; yield 9.193 g (quantitative). The sample (928 mg) used for spectral analysis was purified by placing it on a column containing silica gel (Merck No. 60, 70–230 mesh) which was eluted with 3:1 dichloromethane–ether to afford 871 mg of pure product; it was dried in vacuo for 12 h at 50 °C: $[\alpha]^{24}_D$ +21.5° (*c* 1.1, chloroform); NMR data see Figures 1, 3, and 4 and Table I; signals observed in acetone-d_6 (~20 °C) at δ 0.97 (12 H, 4 closely spaced singlets, CMe_2) and 1.79 (2 H, multiplet, $CCHC_2$) were attributed to the two isobutyl groups in slightly different magnetic environments; the signals for the CH_2 portion of the isobutyl group were overlapped by the solvent resonance.

Anal. Calcd for $C_{21}H_{36}O_8S_2$: C, 52.47; H, 7.56; S, 13.34. Found: C 52.29; H, 7.60; S, 13.45.

Acknowledgment. The authors thank Mr. H. Reutenauer of the Groupe Grenoblois de Résonance Magnétique à Haute Fréquence for recording the NMR spectra.

Registry No.—1, 35304-00-8; D-ribose diisobutyl dithioacetal, 66290-78-6.

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A New Preparation of Triarylsulfonium and -selenonium Salts via the Copper(II)-Catalyzed Arylation of Sulfides and Selenides with Diaryliodonium Salts

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In support of our recent work involving the development of photoinitiators for cationic polymerization, we required a general method for the preparation of pure triarylsulfonium salts. Although the literature contains a number of synthetic procedures for the preparation of these compounds,[1-8] these routes were deemed unsatisfactory for our purposes due to their poor yields, high degree of complexity, long reaction times, or general lack of applicability to a wide variety of substituted symmetrical and unsymmetrical triarylsulfonium salts.

In 1957, Nesmeyanov and his co-workers[9,10] reported that diphenyl sulfide could be directly arylated using diphenyliodonium fluoroborate at 220–230 °C to give triphenylsulfonium fluoroborate (eq 1).

$$(C_6H_5)_2S + (C_6H_5)_2I^+BF_4^- \xrightarrow{220\text{–}230\ °C} (C_6H_5)_3S^+BF_4^- + C_6H_5I \quad (1)$$

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Table I. The Preparation of Various Triarylsulfonium Salts[a]

$$Ar_2I^+X^- + (C_6H_5)_2S \longrightarrow Ar(C_6H_5)_2S^+X^- + ArI$$

	Ar	X^-	registry no.	% yield of $Ar(C_6H_5)_2S^+X^-$	registry no.	mp, °C
I	C_6H_5	BF_4^-	313-39-3	94	437-13-8	191–193[b]
II	C_6H_5	AsF_6^-	62613-15-4	97	57900-42-2	195–197
III	4-*t*-Bu-C_6H_4	PF_6^-	61358-25-6	92	66482-56-2	133–136
IV	4-*t*-Bu-C_6H_4	SbF_6^-	61358-23-4	65	66482-55-1	oil
V	4-*i*-$C_3H_7C_6H_4$	AsF_6^-	62061-12-5	88	66482-53-9	151–152
VI	4-CH_3-C_6H_4	PF_6^-	60565-88-0	87	66482-51-7	174–176
VII	4-C_2H_5-C_6H_4	AsF_6^-	66482-60-8	100	66482-50-6	151–153
VIII	3,4-di-CH_3-C_6H_3	AsF_6^-	66482-58-4	89	66482-48-2	143–145
IX	4-Cl-C_6H_4	AsF_6^-	60635-26-9	94	66482-47-1	130–133

[a] Satisfactory analytical values (±0.3% for C, H, S) were reported for all the compounds in this table. [b] Lit.[11] mp 190–191 °C.

Using a fivefold molar excess of diphenyl sulfide, they obtained a 60% yield of the sulfonium salt. When the same reaction was carried out for 35 h at 180 °C, Knapcyzk and McEwen obtained a slightly better yield (64%).[11] Attempts to prepare substituted triarylsulfonium salts using this method resulted in poor yields of the desired compounds. Our chief concern with this approach to the synthesis of triarylsulfonium salts was its apparent rather limited preparative scope which presumably was related to the severity of the reaction conditions employed.

Recently, the observation was made in our laboratories that diaryliodonium salts possessing nonnucleophilic counterions such as BF_4^-, AsF_6^-, and PF_6^- undergo thermolytic decomposition at temperatures as low as 120–130 °C in the presence of catalytic amounts of a copper(II) compound. In the absence of a catalyst, these compounds decompose at or near their melting points in the range 220–250 °C. Prior to our work, Beringer and his co-workers[12,13] had made the observation that copper(I) and -(II) compounds catalyze the decomposition of diaryliodonium halides in solution. In water or methanol the major products were the aryl halides and the aryl iodide (eq 2).

$$Ar_2I^+Cl^- \xrightarrow{CuCl} ArI + ArCl \qquad (2)$$

It was proposed that the reaction involved the concerted collapse of a complex formed between the diaryliodonium ion and a di- or trichlorocuprate(I) ion. Similarly, Caserio, Glusker, and Roberts[14,15] have reported that the hydrolysis of diaryliodonium tosylates and trifluoroacetates to aryl halides and phenols is strongly catalyzed by traces of copper(I) and -(II) compounds. During the reaction, copper(II) is reduced to copper(I) whose catalytic activity was ascribed to its ability to function as an electron transfer agent.

On the basis of these observations, it was decided to investigate the possibility that copper compounds might catalyze the arylation shown in eq 1. In a model reaction, stoichiometric amounts (0.025 mol) of diphenyl sulfide and diphenyliodonium hexafluoroarsenate were heated together at 120–125 °C under nitrogen for 3 h in the presence of a small amount (7×10^{-4} mol) of copper(II) benzoate. After removing the iodobenzene by-product by washing with ether, the remaining insoluble product was examined by NMR spectroscopy. The product was found to be identical in all respects with an authentic sample of triphenylsulfonium hexafluoroarsenate. It was contaminated only with trace amounts of copper compounds. A yield of 97% of the sulfonium salt was obtained. Repeating the same experiment but omitting the copper benzoate produced no sulfonium salt and only starting materials were recovered.

There is a strong dependence of this reaction on the counterion associated with the diaryliodonium salt. When diaryliodonium halides are used the reaction fails. For example, the reaction of 4,4′-dimethyldiphenyliodonium chloride with diphenyl sulfide in the presence of a catalytic amount of copper(II) benzoate yields only 4-iodotoluene and 4-chlorotoluene and no triarylsulfonium salt. It is, therefore, essential to the success of this reaction that the counterion associated with the diaryliodonium cation be nonnucleophilic in character to avoid competition with the weakly nucleophilic diaryl sulfide for the aryl group.

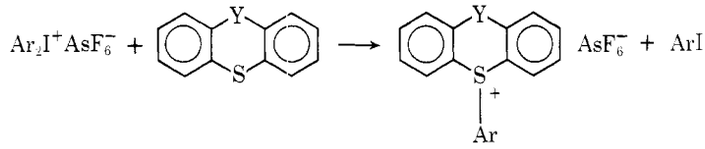
Along with copper compounds, Beringer and his co-workers[13] reported that titanium(II) and chromium(II) chlorides are active catalysts for diaryliodonium halide decomposition. We have found that the above compounds and in addition iron(III) chloride, silver nitrate, cobalt(II) acetate, and palladium(II) acetate do not function as catalysts in the diaryliodonium salt arylation of diaryl sulfides. On the other hand, copper compounds in general do catalyze this reaction. Among those which we have employed successfully are copper(I) chloride and copper(II) acetylacetonate as well as copper(II) acetate, benzoate, and stearate.

Employing a variety of different diaryl sulfides and diaryliodonium salts, it was possible to prepare a considerable number of symmetrical and unsymmetrical triarylsulfonium salts in good to excellent yields. Triarylselenonium salts are also readily accessible via this route from the diarylselenonium compounds. In Tables I–III are given the structures of these compounds along with their yields and melting points. The direct arylation of diaryl sulfides with diaryliodonium salts provides a very convenient synthetic route to the synthesis of triarylsulfonium salts containing condensed ring systems (X–XV). The few compounds of this type which do appear in the literature were prepared in considerably lower yields via a several step synthesis.[16,17]

The precise mechanism by which arylation is catalyzed by copper in these reactions is not understood at this time. Analysis of the ether soluble portion of the reaction mixture by GLC reveals the presence of only the iodoaromatic compound derived from the iodonium salt. Typical radical products such as aromatic hydrocarbons and biphenyl derivatives are not present.

All the reactions used to prepare the compounds appearing in Tables I–III were carried out as neat mixtures of the reactants. Solvents such as dimethylformamide, chlorobenzene, and tetrachloroethane have also been used with equally satisfactory results. Full UV and ^{13}C spectral data for the compounds in Tables I–III are available and appear as Tables IV and V in the microfilm edition. The character of the anion, BF_4^-, PF_6^-, AsF_6^-, or SbF_6^-, has no effect on the position or intensity of the UV absorption bands or on the ^{13}C chemical shift values. The NMR assignments were made on the basis

Table II. The Preparation of Various Heterocyclic Triarylsulfonium Salts[a]



	Ar	registry no.	Y	registry no.	% yield of sulfonium salt	registry no.	mp, °C
X	C_6H_5		O	262-20-4	79	66482-81-3	165–168
XI	4-*i*-C_3H_7-C_6H_4		O		41	66482-80-2	126–127
XII	4-CH_3-C_6H_4	61245-67-8	CH_2	261-31-4	95	66482-78-8	165–167
XIII	4-Cl-C_6H_4		O		99	66482-76-6	183–187
XIV	4-*t*-Bu-C_6H_4	61267-45-6	CH_2		67	66482-73-3	182–185
XV	C_6H_5		CH_2		87	66482-71-1	195–198

[a] Satisfactory analytical values (±0.3% for C, H, S) were reported for all the compounds in this table.

Table III. The Preparation of Various Triarylselenonium Salts[a]

$Ar_2I^+AsF_6^- + (C_6H_5)_2Se \longrightarrow Ar(C_6H_5)_2Se^+AsF_6^- + ArI$

	Ar	$Ar(C_6H_5)_2Se^+AsF_6^-$	registry no.	mp, °C
XVI	C_6H_5	90	57900-43-3	185–187
XVII	4-*t*-Bu-C_6H_4	87	66482-70-0	151–152
XVIII	4-CH_3-C_6H_4	62	66482-68-6	105–110
XIX	3,4-di-CH_3-C_6H_3	49	66482-66-4	103–111

[a] Satisfactory analytical values (±0.03% for C, H, Se) were reported for all the compounds in this table.

of partial decoupling experiments, the relative intensities of the absorptions, and consideration of molecular symmetry as well as comparison with the chemical shift assignments of the parent triphenyl substituted compounds. In all cases, the aromatic ring carbon atoms bonded directly to sulfur or selenium appear at highest field being strongly deshielded by the positively charged heteroatom.

Experimental Section

General. Melting points were determined on a Thomas-Hoover apparatus in open capillaries and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. GLC analyses were recorded on a Hewlett-Packard 5750A gas chromatograph equipped with a 6 ft × 0.25 in. UCW98 silicone column. Proton magnetic resonance spectra were determined with a Varian T-60 spectrometer using tetramethylsilane as an internal standard. Carbon-13 NMR spectra were obtained using a Varian Model XL 100 spectrometer equipped with a broad-band decoupler and a Fourier transform accessory.

Diaryl sulfides, diaryl selenides, and inorganic salts were used as purchased from commercial sources.

General Preparation of Diaryliodonium Salts. The following procedure for the synthesis of diphenyliodonium salts is illustrative of the method used for all of the diaryliodonium salts used in this work. It is adapted from a method described earlier by Berry and his co-workers.[18]

Into a 500-mL three-neck round-bottom flask equipped with a paddle stirrer, addition funnel, thermometer, and condenser were placed 100 g (0.46 mol) of potassium iodate, 100 mL of acetic anhydride, and 90 mL (1 mol) of benzene. This mixture was cooled to −5 °C and then a solution composed of 70 mL of concentrated sulfuric acid and 100 mL of acetic anhydride was added dropwise via the addition funnel. During the addition, the temperature was not permitted to rise above 5 °C. When the addition had been completed, the reaction mixture was allowed to rise to room temperature. After standing for 48 h, the reaction mixture was again cooled to 5 °C and then 200 mL of distilled water was added at such a rate that the reaction temperature did not exceed 10 °C. At this point, 75 mL of diethyl ether was added and the reaction mixture was filtered to remove $KHSO_4$. The aqueous layer was then extracted with diethyl ether and once with petroleum ether. The aqueous solution containing diphenyliodonium bisulfate was then treated in several ways to produce the BF_4^-, AsF_6^-, SbF_6^-, and PF_6^- salts.

Diphenyliodonium fluoroborate was prepared by adding to the aqueous solution 53.5 g (1 mol) of NH_4Cl and isolating the precipitated diphenyliodonium chloride by filtration. Fresh Ag_2O was prepared by mixing equimolar aqueous solutions of $AgNO_3$ and NaOH together and then decanting the aqueous solutions from the precipitated black Ag_2O. The Ag_2O was then washed several times with distilled water and filtered. Next, 20 g of moist Ag_2O, 31.6 g of diphenyliodonium chloride, and 10 mL of water were mixed together in a glass mortar. The reagents were thoroughly ground together until no trace of the iodonium compound could be discerned. The black slurry was then washed into a sintered glass filter and the precipitate was washed with water until 360 mL of filtrate was obtained. After transferring the filtrate to an Erlenmeyer flask, the contents was then frozen into a dry ice–acetone bath and then 25 mL of 45% HBF_4 was added in two portions with stirring. The reaction mixture was allowed to slowly warm to room temperature and then filtered to collect the diphenyliodonium fluoroborate. The salt was dried in vacuo to give 22.1 g (60% yield) of pure product having a melting point of 136 °C (lit.[14] mp 136 °C).

The corresponding AsF_6^-, SbF_6^-, and PF_6^- salts were prepared by adding 0.46 mol of either $KAsF_6$, $KSbF_6$, or KPF_6 in 300 mL of water to the aqueous diphenyliodonium bisulfate solution instead of NH_4Cl. After stirring for 1 h, the crystalline diaryliodonium salt was filtered, washed with water, and dried in vacuo at 60 °C. The salts were recrystallized from isopropyl alcohol. Yields obtained were from 40 to 60%. The following melting points were recorded: AsF_6^- salt, mp 123–125 °C; SbF_6^- salt, mp 57–58 °C; PF_6^- salt, 138–140 °C.

General Procedure for the Arylation of Diaryl Sulfides and Diaryl Selenides. The following general procedure has been successfully employed for the synthesis of all the sulfonium and selenonium salts shown in Tables I–IV. Equivalent amounts (0.025 mol) of the diaryliodonium salt and diaryl sulfide or diaryl selenide and 0.2 g (6×10^{-4} mol) copper benzoate were placed in a 50 mL, single-necked flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen by-pass. The reaction mixture was heated at 120–125 °C in a thermostated silicone oil bath for 3 h. On cooling, the semisolid or crystalline product was washed several times with ether to remove the iodonated aromatic hydrocarbon by-product. The product, although light tan in color due to the presence of traces of copper-containing compounds, is normally quite pure as determined by NMR. Recrystallization from 95% ethanol or 2-propanol gives the colorless pure sulfonium or selenonium salt.

Registry No.—$(C_6H_5)_2S$, 139-66-2; $(C_6H_5)_2Se$, 1132-39-4.

Supplementary Material Available: UV and ^{13}C data for compounds I to XVII, Tables IV and V (3 pages). Ordering information is given on any current masthead page.

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Proton and Carbon-13 Nuclear Magnetic Resonance Study of the Atropisomeric Forms of 4,4,9,17-Tetramethyl-2,6-dithia[7.1]paracyclophane and Its Tetraoxide

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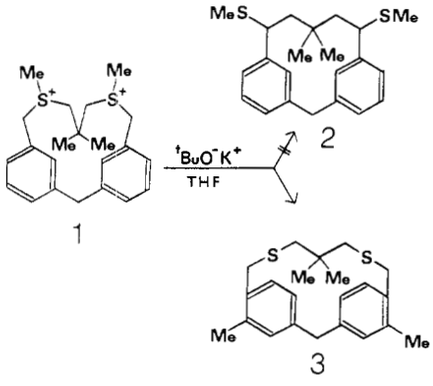
We were intrigued by the recent report of Finch, Gemenden, and Korzun[1] that the attempted Stevens rearrangement of the bissulfonium salt of 4,4-dimethyl-2,6-dithia[7.1]metacyclophane, **1,** did not provide a route to the [5.1]metacyclophane, **2,** but instead yielded the double Sommelet rearrangement product, viz., 4,4,9,17-tetramethyl-2,6-dithia[7.1]paracyclophane, **3.**



Furthermore, the time-dependent ^1H NMR spectra of **3** have been interpreted in terms of an initial anti atropisomer, **3a,** with the *gem*-dimethyl group "inside" the molecular framework, and consequently experiencing some shielding owing to the proximity of the aromatic rings. The formation of the syn atropisomer, **3b,** was deduced from the appearance of two new methyl singlets, one resonating at higher field than Me_4Si, while the intensity of the original *gem*-dimethyl singlet concomitantly decreased.

This fascinating result poses several problems, e.g., why is the Sommelet rearrangement leading to a sterically rigid molecule preferred to the Stevens which would have given a relatively less strained molecule? Does this system allow the investigation of anomalous ^{13}C NMR chemical shifts brought about by ring currents and/or related effects?

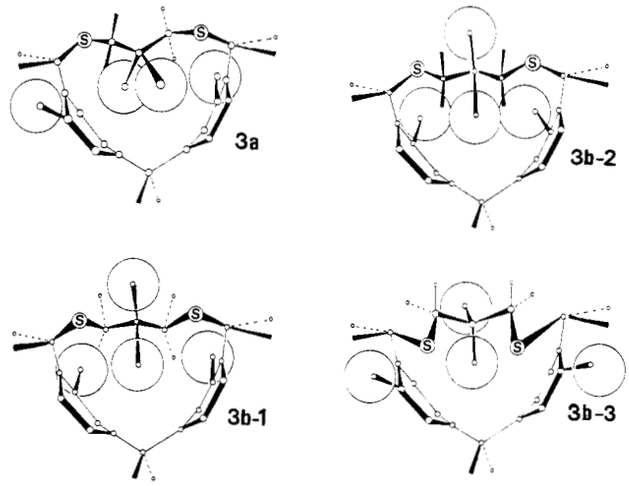


Figure 1. Possible molecular conformations of the atropisomeric forms of **3.**

Our investigation has confirmed the original ^1H NMR observations of Finch et al.,[1] but we have serendipitously obtained evidence for a third atropisomer of **3** not previously reported.

Results and Discussion

The ^1H NMR spectrum of the initial atropisomer, **3a,** is consistent with a molecule of C_2 symmetry such as that depicted in Figure 1. Such a structure accounts not only for the *gem*-dimethyl singlet but also the AB quartets exhibited by the methylene groups at $C_{1,7}$ and $C_{3,5}$. It is noteworthy that the *gem*-dimethyl protons and also the methylene protons at $C_{3,5}$ are considerably upfield of the positions one would normally have anticipated; these upfield shifts for protons positioned above aromatic rings have traditionally been rationalized solely in terms of a ring current model.[2,3] However, recent work[4,5] has elucidated the major contributions made by local anisotropic effects.

Now, the formation of the syn atropisomer, **3b,** must proceed via the rotation of one of the benzene rings with appropriate adjustment of the seven-membered bridging moiety to produce eventually a molecule of C_s symmetry, as required by the ^1H NMR spectrum. It is possible to construct a number of conformations for the syn atropisomer and some of these are shown in Figure 1. **3b-1** shows the most obvious product whereby rotation of an aromatic ring (with the aromatic methyl of necessity remaining on the "outside" of the molecule) pushes the *gem*-dimethyl group such as to place one C_4-methyl group directly above both aromatic rings (and thus receive an extraordinarily high shielding) while the other C_4-methyl moves "outside". However, examination of molecular models shows that a conformation such as **3b-1** provides little hindrance to the continued rotation of the *gem*-dimethyl moiety leading eventually to the third atropisomer, **3c,** in which both *gem*-dimethyl groups are "outside". This would imply that the activation energy barrier between **3b** and **3c** should be small and thus readily overcome at room temperature. However, the transition from the intermediate to the final product requires heat or an extended time interval and hence steric restraints in the intermediate atropisomer appear to be present. One should mention here that molecular models clearly demonstrate that the benzene rings show considerable deviation from planarity, but such effects are not uncommon in cyclophanes.[6,7]

Another possibility, **3b-2,** to be considered is that the aromatic methyls and the *gem*-dimethyl group are on the same

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