

[2₆](1,2,4,5)Cyclophane (Deltaphane) and Related Compounds. Simultaneous π -Electron Interaction among Three Benzene Rings

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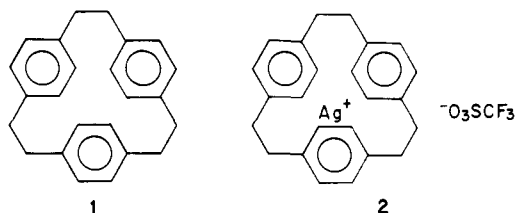
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Abstract: Gas-phase pyrolysis of benzo[1,2;4,5]dicyclobutene (**4**) in a nitrogen stream at 425 °C gives [2₄](1,2,4,5)cyclophane (**7**), [2₆](1,2,4,5)cyclophane (**10**, deltaphane), and 14,20-dimethyl[2₂](1,2,4,5)(1,3,4)(1,3,4)cyclophane-17-ene (**11**). The structures and geometry of **10** and **11** were determined by single-crystal X-ray analysis. Deltaphane (**10**) is of interest because its rigid framework forces the three benzene rings into close proximity with a face-to-face geometry making possible π -electron delocalization among all three rings. Studies of some of the physical and chemical properties of **10** have been made. In view of the report by Pierre et al. that [2₃](1,4)cyclophane (**1**) forms a complex having silver ion held in the cavity of the cyclophane moiety, we prepared the silver triflate complex (**20**) of deltaphane. Variable-temperature NMR studies of solutions of **20** show the silver ion to be undergoing rapid exchange, and an X-ray crystallographic analysis of **20** shows the silver ion to be symmetrically complexed exterior to the deltaphane moiety. A similar examination of the silver triflate complex (**2**) of [2₃](1,4)cyclophane shows the silver ion in this case also to be exterior to the cyclophane moiety and undergoing rapid exchange in solution. Cohen-Addad et al. have recently reported X-ray crystallographic data that are in agreement with these latter observations.

Cyclophanes having three or more arene units contained in medium or large rings have long been studied by chemists. The ortho cyclophanes, including tri-*o*-thymotide,² the salicylides,^{3,4} and anthranilides,⁵ attracted early attention because of the ease with which they formed inclusion compounds. Interest in agents for complexation blossomed with investigations of meta cyclophanes leading to the calixarenes of Gutsche,⁶ and the spherands,⁷ hemispherands,⁸ and cavitands of Cram.⁹⁻¹¹ Among the purely hydrocarbon members, Jenny prepared a series of [2_{*n*}](1,3)-cyclophanes,¹² of which [2₆](1,3)cyclophane was found to form inclusion compounds with a wide variety of substrates.¹³ Baker and others have synthesized [2₃](1,4)cyclophane (**1**),¹⁴⁻¹⁷ and Wennerström has explored some of the higher members of the [2_{*n*}](1,4)cyclophanes.^{18,19}

For exploration of host-guest relationships, or the interaction of π -electron systems, rigidity of the molecular framework is highly desirable. Introduction of additional bridging is one way to accomplish greater rigidity of cyclophanes. For examples, a Fisher-Taylor-Hirschfelder model of [2₆](1,2,4,5)cyclophane (Figure

1) shows the molecule to be rigid, highly symmetrical, and with the three benzene rings held face-to-face to each other at a relatively short distance.²⁰ The possibility of simultaneous π -electron delocalization among its three aromatic rings made [2₆](1,2,4,5)cyclophane (deltaphane²⁰) an attractive molecule for synthesis and for a study of its properties. While work was in progress directed toward this end, Pierre et al. reported the preparation of the silver triflate complex (**2**) of [2₃](1,4)cyclophane and claimed that [2₃](1,4)cyclophane (**1**) was the first member of a new class of compounds for which they proposed the name " π -prismands".²¹ This claim enhanced our interest in deltaphane,



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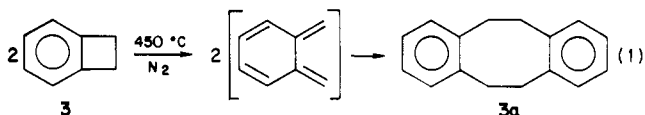
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since it appeared that deltaphane would be a near-ideal " π -prismand".

In our studies on the syntheses and properties of multibridged [2_{*n*}]cyclophanes,^{22,23} we had developed the *o*-xylylene dimerization reaction as a general method for introducing multiple bridges in a single step. In particular, we had found that the gas-phase dimerization of benzocyclobutenes (**3**) in a nitrogen stream was an efficient method for making dibenzocyclooctadienes (**3a**) (eq 1).^{24,25} Presumably, the advantage of carrying out this pyrolysis



in a nitrogen stream at atmospheric pressure is that it allows for control of the concentration of the reactive *o*-xylylene intermediate

(20) An end-view silhouette of [2₆](1,2,4,5)cyclophane, as shown in Figure 1, suggests the Greek letter δ , and so we propose the trivial name deltaphane for the molecule. The cyclophane nomenclature used throughout the manuscript follows and, in some instances, extends, the suggestions for [2₄]cyclophane nomenclature made in ref 23.

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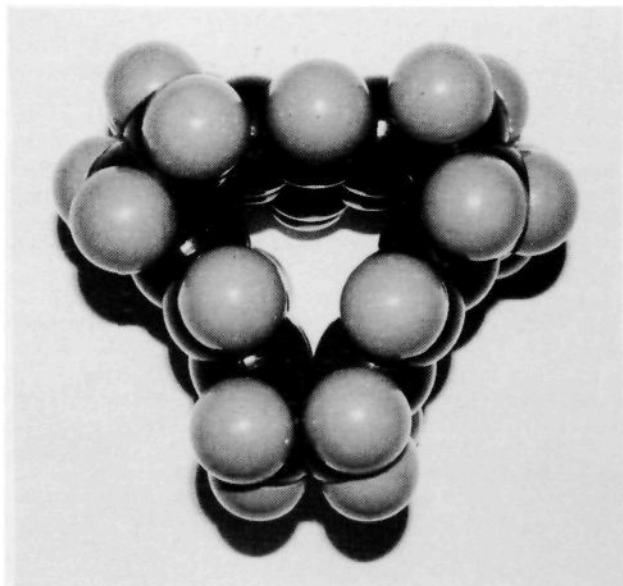
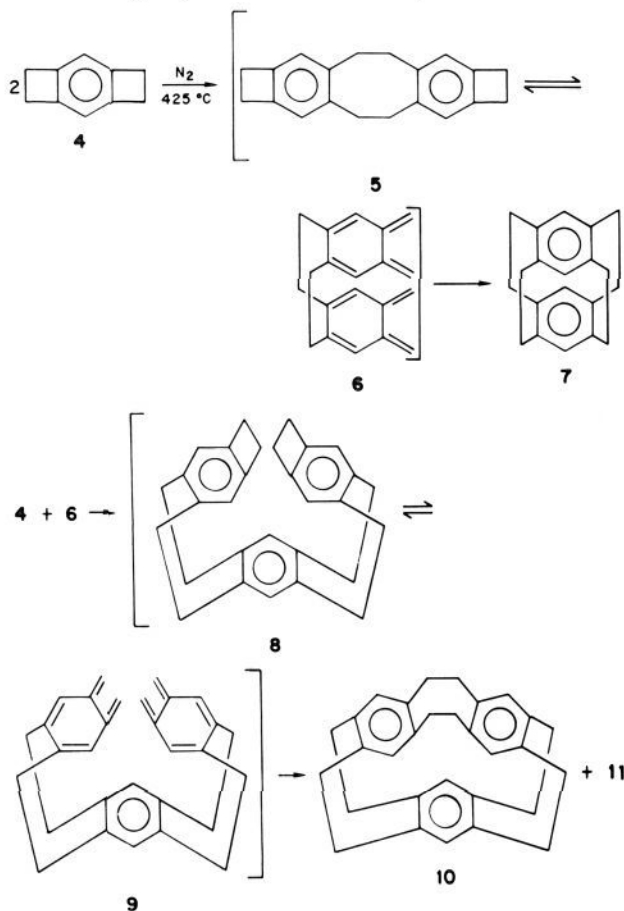


Figure 1. Fisher-Taylor-Hirshfelder molecular model (end view) of $[2_6](1,2,4,5)$ cyclophane (**10**).

so that sufficient bimolecular collisions can be generated to permit formation of the dibenzocyclooctadiene in high yield.

When benzo[1,2:4,5]dicyclobutene (**4**) was employed under similar pyrolysis conditions, $[2_4](1,2,4,5)$ cyclophane (**7**) was obtained conveniently in synthetically useful quantities.²⁵ Presumably, **5** and **6** are intermediates in this pyrolysis. To extend this route to a synthesis of $[2_6](1,2,4,5)$ cyclophane (**10**) the obvious experiment to try was increasing the concentration of **4** in the hot zone of the pyrolysis tube. This should promote bimolecular



collisions between **4** and **6** which could then generate successively

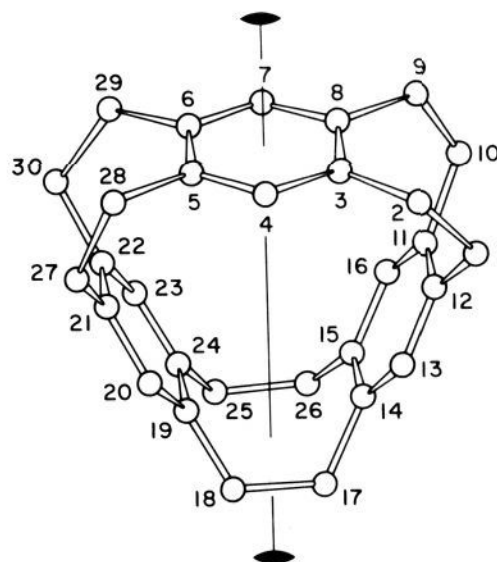


Figure 2. Crystal structure of $[2_6](1,2,4,5)$ cyclophane (**10**, deltaphane). Mean bond lengths: ring (3-4, etc.), 1.390 Å; bridge (1-2, etc.), 1.515 Å; bridgehead (2-3, etc.), 1.505 Å. (Esd's, $\times 0.003$ Å.) Torsion angles of bridging bonds: 1-2, 17°; 9-10, 14°; 17-18, 4°.

intermediates **8** and **9**, leading finally to the desired deltaphane (**10**). This, in fact, occurred. In a typical experiment, pyrolysis of **4** in higher concentrations in a nitrogen stream at 425 °C yielded $[2_4](1,2,4,5)$ cyclophane (**7**, 2.6%), $[2_6](1,2,4,5)$ cyclophane (**10**, deltaphane, 2.3%), and **11** (7.2%).

Deltaphane is a highly insoluble compound, forming pale-yellow crystals melting above 345 °C dec. Its ^1H NMR spectrum shows a singlet at δ 6.30 for the six aromatic protons and an AA'BB' pattern for the bridging methylene protons. The high symmetry of the molecule is also evident from its ^{13}C NMR spectrum which shows only three signals at δ 32.1, 130.9, and 136.7, corresponding to the three types of carbon atoms present.

Confirmation of the structure of **10** and a determination of its geometry was made by a single-crystal X-ray analysis. A summary of the bond lengths and bond angles present in deltaphane is given in Figure 2. The carbon atoms lie essentially in three planes mutually inclined at 120°. The molecule has twofold rotation symmetry, deviating from ideal $\bar{6}m2$ symmetry by a twisting of the bridging methylene carbons to relieve nonbonded hydrogen-hydrogen interactions. Crystal and refinement data for deltaphane are given in Table I.

The ultraviolet absorption spectrum of deltaphane shows band at λ_{max} 274 nm (ϵ 2000) and 283 (1600) with a tailing of absorption out beyond 400 nm. This tailing absorption is responsible for the yellow color of deltaphane and presumably is related to the simultaneous π -electron delocalization among the three benzene rings. Deltaphane also forms a deep purple color with tetracyanoethylene with the charge-transfer complex having an absorption maximum at 485 nm.

Formylation of deltaphane (**10**) via the Rieche procedure²⁶ readily gave the monoaldehyde **12** in 80% yield, illustrating the ease of aromatic substitution. Also, deltaphane formed transition metal complexes with the usual capping agents. Irradiation of a solution of (η^6 -*p*-xylene) (η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (**13**)^{27,28} and **10** in dichloromethane led to the iron complex **14**, and warming a solution of **10** and the tris-(acetonitrile) solvate of (η^5 -cyclopentadienyl)ruthenium(II) hexafluorophosphate (**15**)^{29,30} in 1,2-dichloroethane gave the ruthenium complex **16**.

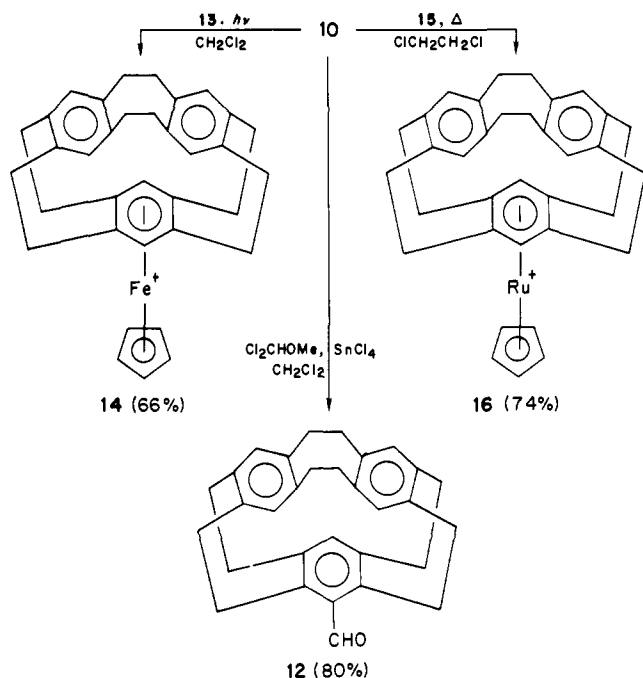
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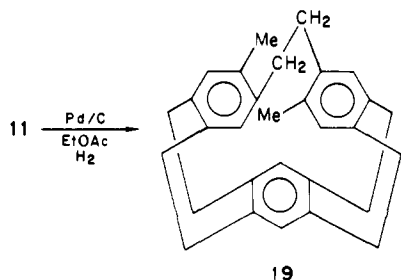
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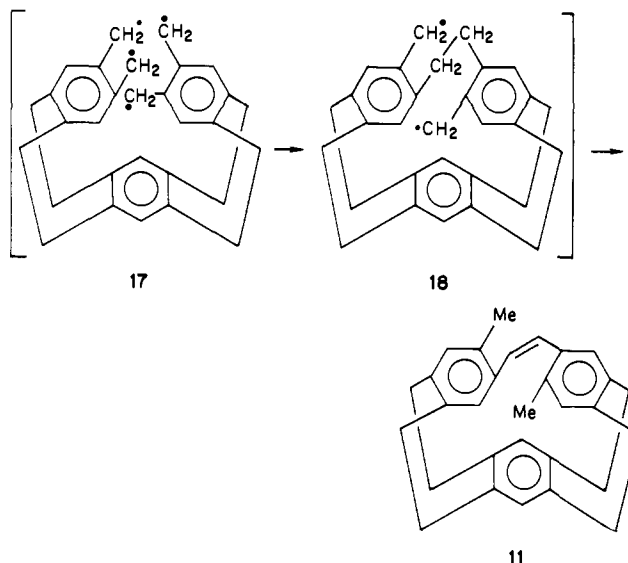
Compound **11**, formed together with **10** during the pyrolysis of **4**, was found by mass spectral analysis to be isomeric with **10**. However, the other spectral properties of **11** were unusual and opened up various possible structures for consideration. For example, the ^1H NMR spectrum of **11** showed three different aromatic singlets of two protons each, a two-proton vinyl singlet, and a six-proton singlet corresponding to two methyl groups. The ^{13}C NMR spectrum of **11** exhibited 15 signals, indicating an element of symmetry leading to five pairs of equivalent aliphatic carbons and ten pairs of equivalent aromatic and vinyl carbons.

Eventually, the structure and geometry of **11** are established by a single-crystal X-ray analysis (see Figure 3). The crystal and refinement data for **11** are given in Table I. As required by its NMR spectra **11** has twofold rotation symmetry. Also, its bond lengths and bond angles are normal and consistent with a strain-free molecule. The presence of the olefinic double bond was confirmed by catalytic hydrogen of **11** to give the corresponding dihydro derivative **19**.



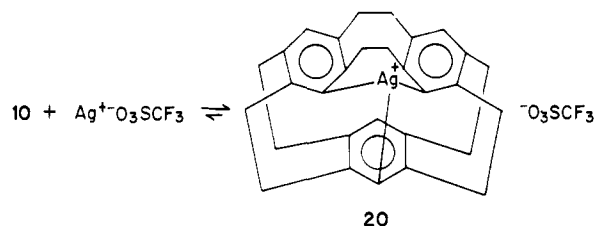
Knowing the structure of **11** one can suggest an obvious path for its formation. Structure **9**, suggested as an intermediate in the formation of deltaphane (**10**), would be expected to have a high degree of radicaloid character. If **9** is rewritten as the tetradical **17**, bond formation between radicals directly opposite to each other would lead to deltaphane. However, bond formation in a diagonal fashion would lead to **18**. This, in turn, by a hydrogen-transfer process would give **11**. What is surprising, though, is that diagonal bond closure to give **11** is preferred over direct bond formation to give deltaphane by a ratio of 3:1.

The rigid geometry of deltaphane (**10**) with its internal cavity circumscribed by three benzene rings seemed ideal for metal ion complexation of the " π -rismand type", as claimed by Pierre et al. for the silver complex of [2₃](1,4)cyclophane (**2**).²¹ Although deltaphane is essentially insoluble in tetrahydrofuran, it rapidly dissolved in tetrahydrofuran containing silver triflate. The silver triflate complex (**20**) of deltaphane can then be isolated and, after



recrystallization from a mixture of chloroform and hexane, is obtained as pale yellow crystals, mp > 330 °C dec.

The conclusion of Pierre et al.²¹ that the silver ion present in **2** is complexed internally within the cavity of the cyclophane moiety, and not externally, was based largely on the temperature invariance and symmetry of the ^1H NMR spectrum of **2**. The room-temperature ^{13}C NMR spectrum of **2** was likewise symmetrical. For the silver triflate complex (**20**) of deltaphane, we found its ^1H NMR spectrum was symmetrical, showing its aromatic protons as a singlet shifted downfield 0.54 ppm from the signal for the aromatic singlet of free deltaphane. However, the ^{13}C NMR spectrum of **20**, a more sensitive test of dynamic processes, showed a symmetrical pattern of three signals at 50 °C, but at -65 °C each of these signals was split giving a six-line spectrum. This clearly established that in solution **20** undergoes



a temperature-dependent dynamic equilibrium at a rate measurable on the NMR time scale.

The dynamic behavior of the NMR solution spectra of **20** prompted an X-ray crystallographic examination of the crystals of the silver triflate complex (**20**) of deltaphane. The structure and geometry of **20** are shown in Figure 4, and the crystal and refinement data for the analysis are given in Table I. The geometry of the cyclophane moiety in **20** is essentially the same as that of the free deltaphane hydrocarbon although the precision of the analysis of the silver complex is unavoidably lower. The silver atom lies an average distance of 2.43 Å from the three nearest carbon atoms, and 0.23 Å from the plane of these atoms on the external side away from the center of the cyclophane moiety. The Ag-C vectors are nearly perpendicular (85°) to the benzene ring planes, and so it follows that the Ag-C interaction must involve primarily the π -electron systems of the benzene rings. This analysis represents an interesting, and somewhat different, situation compared with those of some of the other X-ray analyses of silver complexes of arenes that have been reported.³¹⁻³⁴

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Table I. Crystal and Refinement Data^{a,b}

	10	11	20	2
formula	C ₃₀ H ₃₀	C ₃₀ H ₃₀	C ₃₁ H ₃₀ AgF ₃ O ₃ S	C ₂₅ H ₂₄ AgF ₃ O ₃ S
formula wt	390.6	390.6	647.5	569.4
space group	C2/c (C _{2h} ^s)	P2 ₁ /c (C _{2h} ^s)	P2 ₁ /n (C _{2h} ^s)	P2 ₁ /a (C _{2h} ^s)
a, Å	16.511 (1)	15.934 (1)	18.696 (1)	37.426 (3)
b, Å	9.3886 (4)	9.749 (1)	9.998 (1)	10.448 (2)
c, Å	14.133 (1)	14.066 (1)	14.022 (1)	23.909 (2)
β, deg	108.87 (1)	96.11 (1)	93.37 (1)	90.3 (1)
vol., Å ³	2073.1	2172.6	2616.5	9347.8
Z	4	4	4	16
D _c , g cm ⁻³	1.251	1.194	1.643	1.618
mol symmetry	two-fold rotation			
radiation	Cu	Cu	Mo ^c	Cu
2θ limits, (+h,+k,+l)	4, 130	4, 130	4, 55	4, 110
unique ref scanned	1765	3706	6030	11734
unique ref obsd (I ≥ 3σ(I))	1317	2951	2500	6630
H atoms	refined	refined	assumed	omitted
R (obsd ref)	0.041	0.040	0.053	0.058
k in weighting scheme	0.0005	0.0003	0.001	0.001
R _w	0.060	0.058	0.073	0.081
Error in observation of unit weight	2.03	2.41	1.69	1.78
Esd of C-C bond, Å	0.003	0.002-0.003	0.01-0.02	0.02-0.03

^a At 24 °C (Kα₁): Mo, 0.7093 Å; Cu, 1.54056 Å. ^b Further details, of less general interest, are presented as supplementary data. ^c Cu radiation was used for the unit-cell constants.

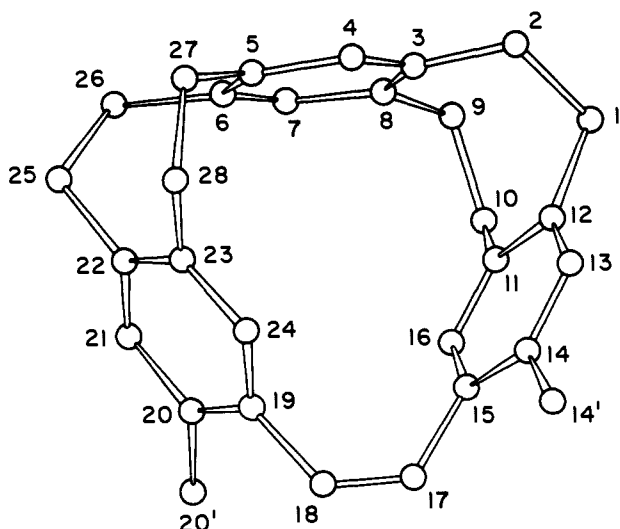
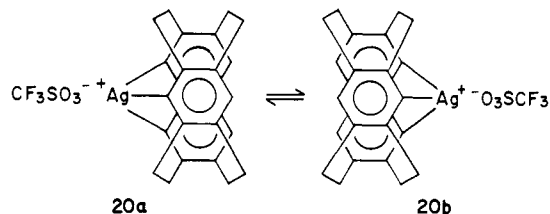


Figure 3. Crystal structure of 14,20-dimethyl[2₅](1,2,4,5)(1,3,4)-(1,3,4)cyclophane-17-ene (11). An approximate two-fold rotation axis passes through the midpoints of 3,6 and 17,18. Mean bond lengths: ring (3-4, etc.), 1.392 Å; bridge (1-2, etc.), 1.548 Å; bridge (17-18), 1.320 Å; bridgehead (2-3, etc.), 1.510 Å; bridgehead (15-17, etc.), 1.481 Å; C-CH₃ (14-14', etc.), 1.508 Å. (Esd's 0.002-0.003 Å.) Bridge torsion angles: 17-18, 3°; others, 32-35°.

If the orientation of the silver ion in the silver-deltaphane complex **20**, as shown in Figure 4, also represents a low-energy conformation for the complex **20** in solution, as is suggested from the NMR data, the dynamic equilibrium in solution must be an equilibrium process between the two enantiomeric conformers **20a** and **20b**. This process, a priori, could occur either by an



external intermolecular exchange or by an interesting intramolecular tunneling of the silver ion through the deltaphane cavity. Since the intermolecular rate process would be affected by changes in concentration, whereas the intramolecular process would not, an easy experimental test was to determine whether the ¹³C NMR

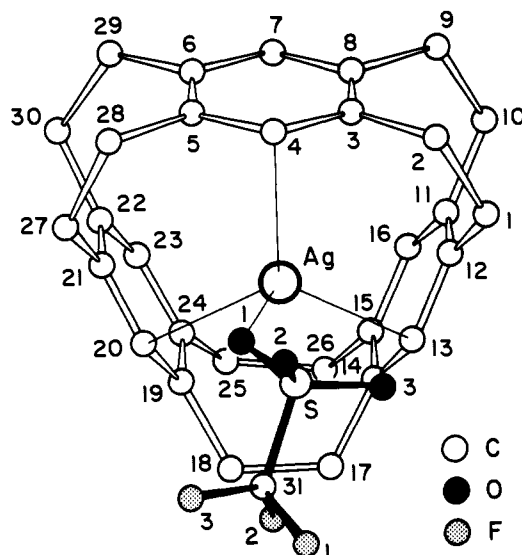


Figure 4. Crystal structure of the silver triflate complex (**20**) of delta-phane. The indicated Ag-C distances range from 2.41 to 2.48 Å (mean, 2.43 Å). The Ag-O distance is 2.49 Å. (Esd's, 0.01 Å.) The torsion angles of the bridging bonds (1-2, etc.) range from -4 to +13°.

coalescence temperature for the exchange process was dependent on concentration. In fact, increasing the concentration of **20** by 30% lowered the coalescence temperature by 10 °C, thus providing a clear indication that the predominant dynamic process for **20** is an intermolecular exchange.

Our finding that silver complexes externally with deltaphane and undergoes rapid intermolecular exchange in solution is in contrast to the previous report of Pierre et al. that the silver ion complex (**2**) of [2₅](1,4)cyclophane has the silver ion in the cavity of the cyclophane moiety. In particular, our finding that the NMR spectrum of **20** is temperature dependent contrasts with their report of the temperature invariance of the ¹H NMR spectrum of solutions of **2**. We repeated their preparation of **2** and, indeed, found its ¹H NMR spectrum for solutions in dideuteriodichloromethane to be as reported and temperature invariant within the experimental range (-80 °C) available. However, the ¹³C NMR spectrum of **2**, taken under similar conditions, showed that the symmetrical, three-line spectrum of **2** at 20 °C undergoes marked line broadening as the solution is cooled to -80 °C, indicating the occurrence of a dynamic equilibrium.

For comparison with the silver triflate complex (**20**) of delta-phane, a crystallographic analysis of the silver triflate complex

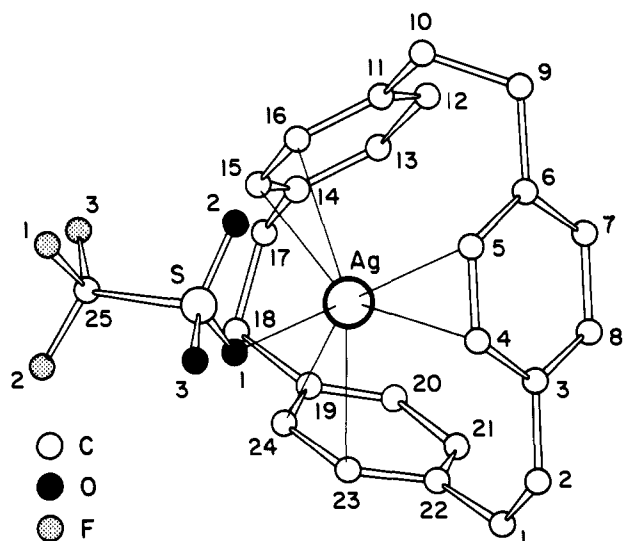
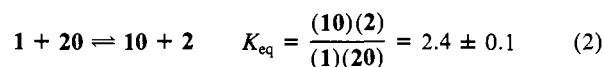


Figure 5. Crystal structure of a representative molecule of the silver triflate complex (**2**) of $[2_3](1,4)$ cyclophane. The indicated Ag-C distances range from 2.40 to 2.69 Å (mean, 2.59 Å). The Ag-O distance is 2.41 Å. (Esd's, 0.01 Å.) The torsion angles of the bridging bonds range from 15 to 55°.

(**2**) was made. The structure and geometry for a representative molecule of **2** are presented in Figure 5 with the crystal and refinement data being given in Table I. Although the accuracy of the analysis is unavoidably low because of the presence of the silver ion, the bond lengths and bond angles for the cyclophane moiety are in accord with its formulation. The cyclophane deviates considerably from $\bar{6}m2$ symmetry, approximating $\bar{3}2$ symmetry by systematic twisting of the bridges. Thus C(1), C(9), and C(17) lie on one side of the bridging bonds, and C(2), C(10) and C(18) lie on the other. The torsion angles of these bonds range from 15 to 55° (mean 42°) and are presumably determined by packing forces. The silver atom lies at an average distance of 2.59 Å from the six nearest aromatic carbon atoms and, thus, about 2.49 Å from the centers of the nearest ring double bonds. The silver atom is external by 0.23 Å from the mean plane of these bonds. The silver triflate complexes, **2** and **20**, have the common structural feature that the silver ion is external to cyclophane moiety and is not present in the "π-prismand cavity". While this work was in progress, Cohen-Addad et al. reported X-ray crystallographic analyses of $[2_3](1,4)$ cyclophane and its silver perchlorate complex.³⁵ Their analysis of the silver perchlorate complex is in close agreement with our findings for the silver triflate complex **2**. They observed that the silver ion in the silver perchlorate complex is 0.24 Å external to the plane containing the centers of the three nearest ring double bonds.

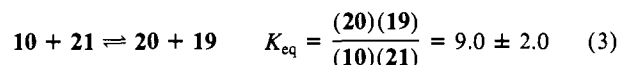
With the establishment that the silver ion in the silver triflate complexes **2** and **20** lies external to the cyclophane moiety in each case and that the silver ion is rapidly exchanging in solution, it was of interest to compare the relative thermodynamic stabilities of the two complexes. This was done by ¹H NMR analyses of the equilibrium concentrations of each of the species present in the reaction of free $[2_3](1,4)$ cyclophane (**1**) with the silver triflate complex (**20**) of deltaphane in deuteriochloroform to give free deltaphane (**10**) and the silver complex (**2**) of $[2_3](1,4)$ cyclophane (eq 2). This allowed the determination of the equilibrium constant



(K_{eq}). As described in the Experimental Section, the equilibrium was approached both starting with **1** and **20** (procedure A) and by starting with **10** and **2** (procedure B). Within experimental error, the value of 2.4 ± 0.1 found for K_{eq} was the same in each

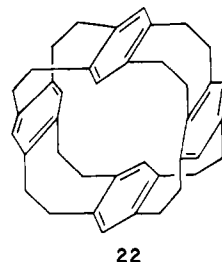
case. The fact that **2** is thermodynamically more stable than **20** suggests that the greater flexibility of the cyclophane moiety in **2** makes possible a better accommodation for the preferred bonding orientation for the silver ion.

Structure **19**, although closely related to that of **10**, has greater flexibility and a larger cavity. It was of interest, therefore, to prepare its silver triflate complex **21** and compare the relative thermodynamic stability of **21** with that of **20**. The equilibrium concentrations (eq 3) were again measured by ¹H NMR analysis



and the equilibrium was approached in two ways. Within experimental error the value of the equilibrium constant was found to be 9.0 ± 2.0 . Apparently, other unknown factors must play an important role.

In summary, the synthesis of deltaphane (**10**) and its derivatives provides examples of a new class of compounds where three benzene rings are held face-to-face in close proximity within a rigid framework. Although the possibility of preparing complexes of deltaphane with a metal ion lodged in the cavity of the cyclophane moiety has not yet been realized, deltaphane and its derivatives do form highly stable silver complexes, and the nature of these complexes has been elucidated. X-ray crystallographic analyses of **10**, **11**, **20** and **2** have been important in providing necessary information regarding the structure and geometry of these molecules. If one regards deltaphane as the first example of rigid cyclophanes having three or more benzene rings, the next higher member of the series is obviously compound **22** having four



benzene rings. Examination of molecular models of **22** indicates that its cavity is large enough not only to accommodate metal ions but also small, rod-like molecules, such as dicyanoacetylene, that form charge-transfer complexes with arenes.

Experimental Section³⁶

Crystallography. Following a preliminary survey of single-crystal photographs, relevant data were measured with a Picker four-circle diffractometer. The unit-cell constants were derived by least-squares analysis of the diffractometer settings of a sufficient number of well-centered high-angle reflections. The relative intensities of the unique reflections were derived by analysis of the profiles recorded during θ - 2θ scans.³⁷ The standard deviations of the intensities were evaluated from counting statistics. Absorption corrections (Gaussian integration) were applied if deemed necessary. The structures were solved by heavy-atom methods if Ag was present, and by direct methods (MULTAN³⁸) otherwise. Refinement of the atomic positions and thermal parameters (anisotropic for non-H atoms) was by block-diagonal least squares, minimizing $\sum w\Delta F^2$, where $1/w = \sigma^2(F_o) + kF_o^2$. H atoms were either disregarded, or included with reasonably estimated or deduced parameters which were either fixed or subsequently refined. Crystal data and pertinent details of data processing and refinement are given in Table I. Further details are presented as supplementary data, together with tables of atomic coordinates and thermal parameters, bond lengths and angles, structure

(36) NMR spectra were measured using a Nicolet NT 360 spectrometer with deuteriochloroform as solvent unless otherwise specified. Mass spectra were obtained with a CEC-21B-110 instrument set at 70 eV. Ultraviolet and visible spectra were taken with a Cary 15 spectrometer. Melting points were measured with a Mel-Temp apparatus and are uncorrected. Elemental analyses are by Dr. R. Wielesek of the University of Oregon Microanalytical Laboratories.

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factors, and some torsion angles and mean plane calculations.

Conventional³⁹ atomic scattering factors, including corrections for the anomalous scattering of Ag and S, were used throughout. The computer program system has been described by Larson and Gabe.⁴⁰

Gas-Phase Pyrolysis of Benzo[1,2,4,5]dicyclobutene (4) To Give [2₄](1,2,4,5)Cyclophane (7), [2₆](1,2,4,5)Cyclophane (10, Deltaphane), and 14,20-Dimethyl[2₅](1,2,4,5)(1,3,4)(1,3,4)cyclophane-17-ene (11). Into a vertical quartz tube (60 × 5 cm) containing 20 g of Pyrex helices at the entrance and held at 425 °C was passed via syringe pump a degassed solution of 5.0 g of benzo[1,2,4,5]dicyclobutene (4) in 45 mL of spectral-grade hexane at a rate of 10 mL/h while a stream of nitrogen was being passed through at 3 mL/s at atmospheric pressure. The exit gases were collected in a cold trap, and the liquid effluent was concentrated under reduced pressure. Sublimation of the resulting solid at 30 °C and 5 × 10⁻³ mm allowed recovery of 600 mg (12%) of benzo[1,2,4,5]dicyclobutene (4). The remaining residual solid was chromatographed over silica gel using hexane for elution.

The first fraction of eluate gave 390 mg of 11 as a pale yellow solid. This was recrystallized from a mixture of dichloromethane and ethyl acetate to provide 360 mg (7.2%) of white prisms: mp 269–270 °C; UV (CH₂Cl₂) λ_{max} 263 nm (ε 7000); ¹H NMR δ 2.30 (6 H, s, CH₃), 2.10–3.40 (16 H, m, CH₂), 5.80 (2 H, s, ArH), 6.27 (2 H, s, ArH), 6.62 (2 H, s, ArH), 6.75 (2 H, s, CH=CH); ¹³C NMR (proton decoupled) δ 19.2, 32.7, 33.1, 36.3, 36.4, 129.0, 130.8, 131.3, 131.5, 133.6, 134.8, 135.5, 136.3, 137.2, 138.6; mass spectrum, *m/e* 390, 260; molecular weight calcd for C₃₀H₃₀ 390.235, found (high resolution mass spectrum) 390.235.

Anal. Calcd for C₃₀H₃₀: C, 92.25; H, 7.75. Found: C, 92.45; H, 7.95.

The second fraction of eluate gave 150 mg of 7 as a pale yellow solid. This was recrystallized to provide 130 mg (2.6%) of white cubes, identical in all respects with an authentic sample of 7.⁴¹

The third fraction, using dichloromethane for elution, gave 140 mg of deltaphane (10) as a yellow solid. This was recrystallized from dichloromethane to give 115 mg (2.3%) of pale yellow crystals: mp >345 °C dec; UV (CH₂Cl₂) λ_{max} 274 nm (ε 2000), 283 (1600) tailing out beyond 400 nm; ¹H NMR δ 2.40–3.25 (24 H, m, CH₂), 6.30 (6 H, s, ArH); ¹³C NMR (proton decoupled) δ 32.1, 130.9, 136.7; mass spectrum, *m/e* 390; molecular weight calcd for C₃₀H₃₀ 390.235, found (high resolution mass spectrum) 390.233.

Anal. Calcd for C₃₀H₃₀: C, 92.25; H, 7.75. Found: C, 92.21; H, 7.97.

Hydrogenation of 14,20-Dimethyl[2₅](1,2,4,5)(1,3,4)(1,3,4)cyclophane (11) To Give 19. A solution of 100 mg of 11 in 60 mL of ethyl acetate was subjected to hydrogenation over a 5% palladium-on-charcoal catalyst under 40 psi of hydrogen for 15 h. After removal of the catalyst and solvent, the residual solid was purified by recrystallization from a mixture of dichloromethane and ethyl acetate to give 98 mg (98%) of 19 as white prisms: mp 305–306 °C; UV (CH₂Cl₂) λ_{max} 270 nm (ε 1600), 279 (1700); ¹H NMR δ 2.32 (6 H, s, CH₃), 2.15–3.30 (16 H, m, CH₂), 5.74 (2 H, s, ArH), 6.28 (2 H, ArH), 6.66 (2 H, s, ArH); ¹³C NMR (proton decoupled) δ 18.6, 32.2, 32.3, 32.5, 35.6, 35.8, 130.2, 130.9, 132.8, 133.0, 135.3, 135.4, 136.5, 136.9, 137.2; mass spectrum, *m/e* 392, 377, 196; molecular weight calcd for C₃₀H₃₂ 392.250, found (high resolution mass spectrum) 392.250.

Anal. Calcd for C₃₀H₃₂: C, 91.78; H, 8.22. Found: C, 92.08; H, 8.36.

Silver Triflate Complex (20) of Deltaphane. To a solution of 33 mg of silver triflate in 25 mL of dry tetrahydrofuran there was added 50 mg of deltaphane (10); the mixture was stirred at room temperature under nitrogen for 0.5 h. After removal of the solvent under reduced pressure, the residual solid was recrystallized from a mixture of dichloromethane and hexane in the dark to give 71 mg (85%) of 20 as pale yellow crystals: mp >330 °C dec; ¹H NMR δ 2.75–3.43 (24 H, m, CH₂), 6.84 (6 H, s, ArH); ¹³C NMR (proton decoupled) at +50 °C δ 31.4, 125.7, 139.3; at -60 °C δ 31.2, 31.5, 117.2, 133.9, 139.2, 139.4.

Anal. Calcd for C₃₁H₃₀F₃O₃SAg: C, 57.50; H, 4.67. Found: C, 57.08; H, 4.97.

Silver Triflate Complex of 11. To a solution of 13 mg of silver triflate in 15 mL of dry tetrahydrofuran there was added 20 mg of 11; the mixture was stirred at room temperature under nitrogen for 0.5 h. After removal of the solvent under reduced pressure, the residual solid was recrystallized from a mixture of dichloromethane and hexane in the dark to give 26 mg (79%) of a white, powdery solid: mp >296 °C dec; ¹H

Table II. Measurement of the Equilibrium Constant for 1 + 20 ⇌ 10 + 2. $K_{eq} = (10)(2)/(1)(20)$

compd	procedure A ^a	procedure B ^a
1	1.17 × 10 ⁻³	1.53 × 10 ⁻³
20	1.60 × 10 ⁻³	1.39 × 10 ⁻³
2	2.36 × 10 ⁻³	2.16 × 10 ⁻³
10	1.95 × 10 ⁻³	2.46 × 10 ⁻³
K_{eq}	2.46 ± 0.10	2.49 ± 0.10

^a See text.

NMR δ 2.37 (6 H, s, CH₃), 2.50–3.45 (16 H, m, CH₂), 6.36 (2 H, s, ArH), 6.72 (2 H, s, ArH), 6.72 (2 H, s, CH=CH), 7.12 (2 H, s, ArH); ¹³C NMR (proton decoupled, at 25 °C) δ 19.5, 32.1, 32.3, 35.2, 35.7, 122.7, 126.4, 131.0, 131.3, 134.8, 136.6, 138.3, 139.5.

Anal. Calcd for C₃₁H₃₀F₃O₃SAg: C, 57.50; H, 4.67. Found: C, 57.86; H, 4.49.

Silver Triflate Complex (21) of 14,20-Dimethyl[2₅](1,2,4,5)(1,3,4)(1,3,4)cyclophane. A solution of 9 mg of 19 and 6 mg of silver triflate in 10 mL of dry tetrahydrofuran was stirred at room temperature under nitrogen for 0.5 h. After removal of the solvent under reduced pressure, the residual solid was recrystallized from a mixture of dichloromethane and hexane in the dark to give 12 mg (80%) of 21 as a white, powdery solid: mp >302 °C dec; ¹H NMR δ 2.44 (6 H, s, CH₃), 2.60–3.40 (20 H, m, CH₂), 6.35 (2 H, s, ArH), 6.77 (2 H, s, ArH), 7.12 (2 H, s, ArH); ¹³C NMR (proton decoupled, at 25 °C) δ 18.8, 31.6, 34.5, 35.1, 125.5, 126.7, 131.4, 134.6, 137.0, 138.4, 138.5, 139.6.

Anal. Calcd for C₃₁H₃₂F₃O₃SAg: C, 57.33; H, 4.97. Found: C, 57.75; H, 4.80.

Formylation of Deltaphane (10) via the Rieche Reaction To Give 12.

To a suspension of 50 mg of deltaphane (10) and 50 μL of stannic chloride in 50 mL of dry dichloromethane held at 0 °C was added 40 μL of dichloromethyl methyl ether with stirring under a nitrogen atmosphere. After the mixture had been stirred at 0 °C for 1 h, it was allowed to warm to room temperature and was stirred for an additional 34 h. Then the reaction mixture was poured into ice-water and extracted with dichloromethane; the dichloromethane extract was washed with water, dried, and concentrated. Purification of the residue by preparative thin-layer chromatography over silica gel using dichloromethane as eluent gave 43 mg (80%) of 12 as pale yellow crystals: mp >281 °C dec; IR (KBr) δ_{max} 2840 (C—H), 1685 (C=O) cm⁻¹; ¹H NMR δ 2.60–3.40 (24 H, m, CH₂), 6.29 (2 H, s, ArH), 6.32 (2 H, s, ArH), 6.51 (1 H, s, ArH), 10.43 (1 H, s, CH=O); mass spectrum, *m/e* 418, 390; molecular weight calcd for C₃₁H₃₀O 418.230, found (high resolution mass spectrum) 418.227.

Anal. Calcd for C₃₁H₃₀O: C, 88.95; H, 7.28. Found: C, 89.05; H, 7.19.

Conversion of Deltaphane (10) to the Corresponding Iron Complex 14.

A degassed solution of 18 mg of (η⁶-*p*-xylene)(η⁵-cyclopentadienyl)iron(II) hexafluorophosphate (13)²⁷ and 20 mg of deltaphane (10) in 50 mL of dry dichloromethane was irradiated with visible light (G.E. reflector flood lamp, 150 W) for 7 h. The reaction mixture was filtered through glass wool before concentration. The resulting solid was stirred with 30 mL of acetone for a few minutes, and then filtered to remove insoluble deltaphane. The filtrate was concentrated to give a yellow solid. This was recrystallized from a mixture of acetone and ether to give 21 mg (66%) of 14 as yellow-bronze crystals: mp >308 °C dec; ¹H NMR (nitromethane-*d*₃) δ 2.50–3.50 (24 H, m, CH₂), 4.68 (5 H, s, Cp), 5.37 (2 H, s, ArH), 6.37 (4 H, s, ArH).

Anal. Calcd for C₃₅H₃₅PF₆Fe: C, 64.04; H, 5.37. Found: C, 64.17; H, 5.25.

Conversion of Deltaphane (10) to the Corresponding Ruthenium Complex 16. A suspension of 10 mg of (η⁵-cyclopentadienyl)ruthenium(II) hexafluorophosphate tris(acetonitrile) solvate (15)²⁹ and 15 mg of deltaphane (10) in 15 mL of 1,2-dichloroethane was boiled under reflux in a nitrogen atmosphere for 15 h. After removal of the 1,2-dichloroethane under reduced pressure, the residual solid was stirred with 20 mL of acetone for a few minutes, and then filtered to remove the insoluble deltaphane. The filtrate was concentrated to give a yellow solid. This was recrystallized from a mixture of acetone and ether to give 12 mg (74%) of 16 as yellow crystals: mp >297 °C dec; ¹H NMR (nitromethane-*d*₃) δ 2.45–3.40 (24 H, m, CH₂), 5.08 (5 H, s, Cp), 5.47 (2 H, s, ArH), 6.46 (4 H, s, ArH).

Anal. Calcd for C₃₅H₃₅PF₆Ru: C, 59.91; H, 5.03. Found: C, 59.69; H, 5.37.

Study of the Relative Thermodynamic Stabilities of Silver Triflate Complexes 2, 20, and 21. Data are given in Tables II & III.

1 + 20. Procedure A. To a solution of 2.3 mg (3.55 × 10⁻³ mmol) of 20 in 2 mL of deuteriochloroform was added 1.1 mg (3.53 × 10⁻³ mmol) of 1; the solution was stirred in the dark at room temperature for

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Table III. Measurement of the Equilibrium Constant for $10 + 21 \rightleftharpoons 20 + 19$. $K_{eq} = (20)(19)/(10)(21)$

compound	equilibrium concentrations, mmol	
	procedure A ^a	procedure B ^a
10	1.01×10^{-3}	2.00×10^{-3}
21	0.77×10^{-3}	0.66×10^{-3}
20	2.58×10^{-3}	2.79×10^{-3}
19	2.77×10^{-3}	4.19×10^{-3}
K_{eq}	9.2 ± 2.0	8.9 ± 2.0

^aSee text.

65 h. The reaction was monitored by ¹H NMR analysis to determine the relative concentrations of each component. No change was evident after 65 h.

Procedure B. To a solution of 2.1 mg (3.69×10^{-3} mmol) of **2** in 2 mL of deuteriochloroform was added 1.5 mg (3.85×10^{-3} mmol) of **10**; the solution was stirred in the dark at room temperature for 65 h. The relative concentrations of the components were monitored by ¹H NMR analysis and showed no change after 65 h.

10 + 21. Procedure A. To a solution of 2.3 mg (3.54×10^{-3} mmol) of **21** in 3 mL of deuteriochloroform was added 1.4 mg (3.59×10^{-3} mmol) of **10**; the solution was stirred for 50 h in the dark at room temperature. The reaction was monitored by ¹H NMR analysis to determine the relative concentrations of each component. No change was evident after 50 h.

Procedure B. To a solution of 3.1 mg (4.79×10^{-3} mmol) of **20** in 3 mL of deuteriochloroform was added 1.9 mg (4.85×10^{-3} mmol) of

19; the solution was stirred at room temperature in the dark for 50 h. The reaction was monitored by ¹H NMR analysis to determine the relative concentrations of each of the components. No change was evident after 50 h.

Variable-Temperature C¹³ NMR Studies of 20. The C¹³ NMR spectrum of the silver complex of **20** was measured using a 2.5×10^{-2} M solution in deuteriochloroform with a Nicolet NT 360 spectrometer. At 20 °C, the spectrum showed a sharp singlet at 31.3 ppm (sp³ carbons), a sharp singlet at 138.7 ppm (sp² carbons), and a broad singlet at 125.5 ppm (sp² carbons bound to Ag⁺). When the solution was cooled, the signals broadened and showed coalescence at near -10 °C. In the range of -50 to -65 °C, the solution showed six sharp singlets at 31.5 and 31.2 (sp³ carbons), 139.3, 138.1, and 133.8 (sp² carbons), and 117.1 ppm (sp² carbon bound to Ag⁺). When these measurements were repeated using a lower concentration (1.89×10^{-2} M), coalescence occurred at approximately 0 °C.

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Registry No. **2**, 94978-61-7; **4**, 1610-51-1; **7**, 54100-59-3; **10**, 94978-50-4; **11**, 94978-47-9; **11**-CF₃SO₃Ag, 94978-54-8; **12**, 94978-49-1; **14**, 94978-58-2; **16**, 94978-60-6; **19**, 94978-48-0; **20**, 94978-52-6; **21**, 94978-56-0; CF₃SO₃Ag, 2923-28-6; Cl₂CHOCH₃, 4885-02-3.

Supplementary Material Available: Details of the X-ray crystal structure analyses including tables of the atomic coordinates and structure factors (117 pages). Ordering information is given on any current masthead page.

Spectroscopy and Photochemistry of Conjugated Nonprotonated Schiff Bases: Application of an ab Initio Derived Heisenberg Effective Hamiltonian

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Abstract: A Heisenberg effective Hamiltonian, previously derived for conjugated hydrocarbons and imines, is extended to treat $n\pi^*$ excited states as well as ground and $\pi\pi^*$ states; this Hamiltonian is applied to the conjugated (nonprotonated) Schiff bases series up to five double bonds. The vertical excitation energies to the neutral excited states are calculated as a function of the chain length and extrapolated to larger systems; the excited-state geometries are optimized by showing the extreme importance and diversity of geometrical relaxations: this problem is illustrated in details for 2-propen-1-imine (allylideneimine) for which accurate MO-CI calculations are available. The 90° twisting of CC double bonds has been investigated in both ground and neutral excited states; the perturbation due to the heteroatom is larger in the excited states than in the ground state. It seems undoubtedly that for large enough polyenimines, the "¹A_g" excited state is lower than the "¹B_u" allowed state and that cis-trans isomerization around internal double bonds is possible on the ¹A_g surface.

1. Introduction

The absorption and photochemical properties of polyenes is an important topic in visible and UV spectroscopy² and a sort-of permanent test field for theoretical models.³⁻⁹ Recently, a new

approach based on the use of a Heisenberg effective Hamiltonian (HEH) has been successfully applied to the study of the photochemistry of linear polyenes, permitting an easy prediction of conformational and energetic properties of some important excited states,¹⁰ a study of rotational barriers in both ground¹¹ and excited states,¹⁰ and an analysis of the photochemical role of the ¹A_g lower

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(2) See, e.g.: (a) Jaffe, H. H.; Orchin, M. "Theory and Applications of Ultraviolet Spectroscopy"; Wiley: New York, 1962. (b) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Wiley: New York, 1963.

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