free energy of activation ($\Delta G_c^{\ddagger}$) at coalescence can then be estimated by using the Eyring equation (eq 2).[13] From

$$k_c = \pi/2^{1/2}(\Delta\nu^2 + 6J^2)^{1/2} \quad (1)$$

$$\Delta G_c^{\ddagger} = 2.303RT_c(10.32 + \log T_c - \log k_c) \quad (2)$$

the conformational studies of **6**, the value of $\Delta G_c^{\ddagger}$ at 225 K was calculated to be 11.0 kcal mol^{-1}. From the respective barriers of the $CH_2CH_2CH_2$ (11.5 kcal mol^{-1}) and CH_2SCH_2 (ca. 10 kcal mol^{-1}) bridge-wobbling processes of **3**, replacement of a CH_2 unit with sulfur seems to lower the barrier by ca. 1.5 kcal mol^{-1}. Introduction of two sulfur atoms such as in **2**, **5**, and **6** would be expected to decrease the conformational barrier to a greater extent. The $\Delta G_c^{\ddagger}$ value of 11.0 kcal mol^{-1} observed for the fluxional process in **6** would then seem too high for such a similar bridge-wobbling behavior. This serves as another indication that the barrier estimated in fact corresponds to the ring flipping process **6a** $\rightleftarrows$ **6a′**/**6b** $\rightleftarrows$ **6b′**.

The detailed study[3] of [3.3]metacyclophane **4** has provided evidence for the bridge-wobbling processes in a [*m.n*]cyclophane; our results on dithia[3.3]orthocyclophane **6**, however, strongly suggest that the observed conformational interconversion involves ring-flipping processes. In yet some other reported examples[15] of [3.3]cyclophanes, absence of ring flipping with wobbling of bridges could seemingly result in very similar chemical shifts (possibly unresolved) for the bridging methylene protons. The above results collectively suggest that DNMR analysis of [*m.n*]cyclophanes may not necessarily reveal an identical fluxional behavior. The observable process or processes would depend on the relative conformational barriers of bridge wobbling and ring flipping, both of which should differ from one [*m.n*]cyclophane to another and in turn depend significantly on the geometry of each cyclophane.

Experimental Section

^{1}H NMR spectra were determined on a JEOL FX90Q (90 MHz) Fourier transform spectrometer. ^{13}C NMR were recorded on a JEOL FX90Q Fourier transform spectrometer operating at 22.5 MHz. All chemical shifts are reported in ppm downfield from tetramethylsilane used as internal standard. IR spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer. UV spectra were recorded on a Shimadzu UV240 Graphicord UV–vis spectrometer. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV with electron impact. Relative intensities are given in parentheses. Dithiametacyclophane **5** was prepared according to reported procedure.[16]

2,11-Dithia[3.3]orthocyclophane (6). A solution of 1,2-bis(bromomethyl)benzene (1.63 g, 6.2 mmol) and 1,2-bis(mercaptomethyl)benzene (1.05 g, 6.2 mmol) in degassed benzene (200 mL) was added dropwise using a rotaflow dropping funnel into a well-stirred solution of KOH (0.86 g, 15.5 mmol) in degassed 95% EtOH (500 mL) under N_2. After the addition, the mixture was stirred for 12 h at room temperature. The bulk of the solvent was then removed under reduced pressure. Dichloromethane and H_2O (1:1, 200 mL) were added, and the mixture was stirred until all solids dissolved. The organic layer was separated, washed with water, dried, and evaporated. The residue was chromatographed on silica gel with dichloromethane/*n*-hexane (1:1) as eluant to give **6**: 1.38 g (82%); mp 244–246 °C (lit.[10] mp 249–251 °C); ^{1}H NMR ($CDCl_3$) δ 7.63–7.49, 7.33–7.18 (m, AA′BB′, 8 H, Ar H), 3.41 (s, 8 H, CH_2S); IR (KBr) 1476, 1440, 1425, 1400, 1216, 1200, 1070, 1038, 945, 912, 825, 808, 765, 702, 664 cm^{-1}; UV (cyclohexane) λ_{max} 211 (ϵ 19000), 241 (5100) nm; MS, $M^{\cdot+}$ *m/z* (relative intensity) 272 (49), 135 (100), 104 (50), 91 (17); M_r calcd for $C_{16}H_{16}S_2$ 272.0693, found (MS) 272.0695.

Acknowledgment. Y.H.L. thanks the National University of Singapore for financial support (RP606/86) of this work. Technical assistance from Mr. Yeo and Miss Wong is also greatly appreciated.

Registry No. **6**, 7215-69-2.

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[15] See, for example: Boekelheide, V.; Hollins, R. A. *J. Am. Chem.* **1973**, *95*, 3201. Lai, Y.-H. *Heterocycles* **1985**, *23*, 2769. Mitchell, R. H.; Vinod, T. K.; Bodwell, G. J.; Weerawarna, K. S.; Anker, W.; Williams, R. V.; Bushnell, G. W. *Pure Appl. Chem.* **1986**, *58*, 15.

[16] Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.

Structures of "Half-Opened" Cyclopropyl Cations. Theoretical Confirmation of Experimental Postulates

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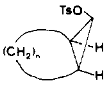
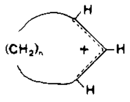
The parent cyclopropyl cation is not a minimum on the potential energy surface.[1] Hence, solvolysis of cyclopropyl derivatives normally leads to concerted disrotatory ring opening with the formation of allyl cation intermediates.[2-4] Woodward and Hoffmann's prediction that the orientation of the leaving group would determine the direction of this rotation, inward or outward,[4] has been verified inter alia by direct observation of the stereochemistry of product ions in superacid media.[5] This disrotational preference can lead to important differences in behavior, especially in bicyclo[*n*.1.0]alkyl systems **1** and **2**. The endo derivatives **1** solvolyze rapidly to give *cis,cis*-allyl cation intermediates **3** with relief of strain. However, as first postulated by Schöllkopf, Schleyer, et al.,[2] the exo derivatives **2** react to give only "partially opened" carbocation intermediates **4**. These arise because the required disrotatory



1



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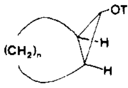

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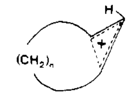

4

compd	rel rate[a]	compd	rel rate[a]
c-$C_3H_5OT_5$[b]	1	**2**, *n* = 3	$10^{-4\,c}$
1, *n* = 3	25 000	**2**, *n* = 4	1.7
1, *n* = 4	62	**2**, *n* = 5	2500
1, *n* = 5	3.1	**2**, *n* = 6	10 000
1, *n* = 6	3.5		

[a] Reference 2. [b] HOAc, 100 °C. [c] Reference 12.

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[1] While the cyclopropyl cation is a minimum at 3-21G (Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P, v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649) and at 6-31G*, the barrier to opening is very small (0.1 kcal/mol at 6-31G*) and disappears at electron correlated levels. Similar conclusions have been reached recently by Taylor et al.: Taylor, C. A.; Zerner, M. C.; Ramsey, B. *J. Organomet. Chem.* **1986**, *317*, 1.

[2] Schöllkopf, U.; Fellenberger, K.; Patsch, M.; Schleyer, P. v. R.; Su, T.; van Dine, G. W. *Tetrahedrom Lett.* **1967**, 3639. Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 588; *Angew. Chem.* **1968**, *80*, 603. Sliwinski, W. S.; Su, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 133.

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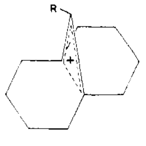
opening would lead to a trans,trans 1,3-disubstituted allyl cation configuration which, for obvious reasons, cannot be fully achieved in ring systems of ordinary size. These postulated "half-opened" cyclopropyl cations were supported by model calculations on $C_3H_5^+$ which showed that the central hydrogen in the cyclopropyl cation moves strongly out-of-plane during the disrotatory opening.[6] Indeed, the solvolyses of exo educts **2** give exo products,[2,3] i.e., with the retention of configuration which characterizes nonclassical carbocation behavior. In addition, the relative solvolysis rates of **2** increase with increasing ring size while the opposite is the case for the corresponding endo series, **1**.[2] Partially opened cyclopropyl cations have been investigated subsequently quite extensively.[3,7]

More recently, Olah and Ledlie have been able to observe a half-open cyclopropyl cation derivative in a tricyclic system (**5**) under stable ion conditions.[7] The substantial deshielding of the ^{13}C NMR signals for C_1, C_6, C_{11} in **5** provides evidence for the nature of this species.



5

We now report the first calculational study of "half-open" cyclopropyl cations **4** (n = 2–5). The corresponding opened cycloallyl cations **3** (n = 2–5) were also examined for comparison. The results confirmed the earlier postulates nicely and provide detailed information concerning the structure of these interesting species for the first time.

The $C_5H_7^+$ and $C_6H_9^+$ cations (**3** and **4**, n = 2 and 3) were calculated at standard ab initio levels,[8] and the entire set was examined with MINDO/3.[9] The smallest bicyclopentyl system (**4**, n = 2) failed to give a minimum energy configuration corresponding to a partially opened cation. Instead, optimization with the split-valence 3-21G basis set starting with a geometry corresponding to **4** (n = 2) led automatically, after a number of cycles, to the cyclopentenyl cation (**3**, n = 2).[10] Experimentally, **2** (n = 2) is known to be essentially inert solvolytically; reaction only occurs via a prior thermal bicyclopentane inversion.[11] The much slower solvolysis rate of **2** (n = 3) than the parent cyclopropyl system[2,12] provides direct evidence for acceleration due to anchimeric assistance in the latter.[13]

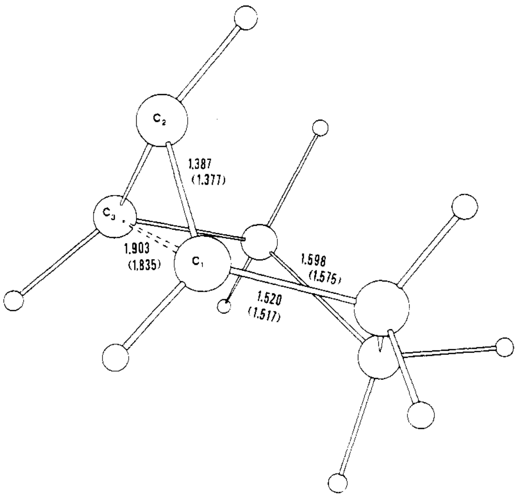


Figure 1. The "half-opened" bicyclo[3.1.0]hexyl cation (**4**, n = 3) calculated at 3-21G (6-31G* parameters are given in parentheses). The hydrogen at C_2 is bent out of the $C_1C_2C_3$ plane by 42.6° (41.7°).

Table I. Comparison of Characteristic Geometrical Features[a]

	$r(C_1C_2)$, Å	$r(C_1C_3)$, Å	$\angle C_1C_2C_3$, deg
allyl cation[b]	1.384 (1.373)	2.384 (2.355)	118.9 (118.1)
cyclohexenyl cation, **3** (n = 3)	1.375	2.371	119.5
half-opened cation, **4** (n = 3)[c]	1.387 (1.377)	1.903 (1.835)	86.6 (83.6)
cyclopropyl cation[b,d]	1.453 (1.439)	1.522 (1.512)	63.2 (63.4)

[a] 3-21G data (6-31G* optimized values in parentheses). [b] *Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie-Mellon University: Pittsburgh, PA, 1983. [c] See Figure 1. Optimization at correlated levels (not currently possible at Erlangen due to technical limitations) should give somewhat shorter C_1C_3 bond lengths.[1,15] [d] The MP2(FULL)/6-31G* optimized values are 1.423 (C_1C_2), 1.529 (C_1C_3), and 65.0°.

Indeed, optimization of the next larger system (**4**, n = 3) did lead to a partially opened cyclopropyl cation at 3-21G, 6-31G* ab initio, and at MINDO/3 levels. The 3-21G geometry, depicted in Figure 1 (the 6-31G*-optimized parameters also are given), shows a number of notable features which may be compared with the ab initio geometries of the allyl and cyclopropyl cations and the isomeric cyclohexenyl cation (**3**, n = 3) (Table I). While the C_1C_2 bond lengths are nearly the same in all three species, the $C_1 \cdots C_3$ distance in **4** (n = 3) is much shorter, and the $C_1C_2C_3$ angle much smaller than the nearly identical values in the allyl cations. In fact, $r(C_1 \cdots C_3)$ and $\angle C_1C_2C_3$ in **4** (n = 3) are just about halfway between the corresponding parameters in the cyclopropyl and allyl cations (Table I). Along with Figure 1, this demonstrates that our description of species like **4** as "half-opened" cyclopropyl cations[2] was apt indeed.

However, **4** (n = 3) is the smallest bicyclic ring system which can be expected to support a "half-opened" cyclopropyl cation. Hence, the structural deviation from a planar allyl cation geometry is expected to be greatest for this system.[13] As is shown by the MINDO/3 results for

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[9] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294.

[10] This result at MINDO/3 has been reported earlier by Jorgensen: Jorgensen, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 6784.

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[14] See: Siam, K.; Ewbank, J. D.; Schäfer, L.; van Alsenoy, C. *J. Mol. Struct.* **1987**, *150*, 121.

[15] The lengths of partial bonds in the nonclassical 2-bicyclo[2.1.1]-hexyl cation (Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300) afford an analogy. These range from 1.992 Å at 3-21G to 1.923 Å at 6-31G* to 1.873 at MP2FU/6-31G*.

Table II. MINDO/3 Geometries and Relative Energies for 3-5 Isomers[a]

species	$r(C_1C_3)$	$r(C_1C_2)$	$\angle C_1C_2C_3$	ΔH_f	rel E
3, n = 3	1.681[b]	1.424[b]	72.3[b]	230.3	0.0
3, n = 4	1.864	1.401	83.4	212.8	0.0
3, n = 5 exo	2.155	1.390	89.6	193.6	0.0
3, n = 5 endo	2.107	1.391	101.6	195.7	2.1
4, n = 3	2.401[b]	1.395[b]	118.7[b]	182.6	47.7[c]
4, n = 4	2.487	1.394	126.2	175.2	37.6
4, n = 5	2.555	1.393	132.9	169.2	24.4
5, C_s endo,exo	2.248	1.413	105.4	194.5	0.0
5, C_s endo,endo	2.266	1.411	106.8	195.2	0.7
5, C_s exo,exo	2.236	1.411	104.8	194.5	0.0
5, C_{2v} endo,endo	1.636	1.452	68.6	210.1	15.6
5, C_{2v} exo,exo	1.625	1.455	67.9	209.9	15.4

[a] Distance in angstroms, angles in degrees, energies in kilocalories/mole. "Exo" and "endo" refer to ring conformations. [b] Compare these values with the ab initio geometries in Table I. [c] The ab initio energy difference is 42.1 kcal/mol using the MP2/6-31G*//6-31G* energy for 3, n = 3 (-232.852 02) and the MP2/6-31G*//3-21G value for 4, n = 3 (-232.919 16). As expected,[8] higher values are obtained when electron correlation corrections are not included (i.e., at 3-21G//3-21G, Δ = 64.6; 6-31G*, Δ = 60.1 kcal/mol).

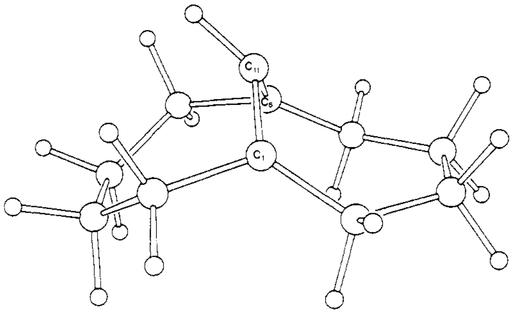

Figure 2. MINDO/3 geometry of the bicyclo[4.4.1]undecyl cation (5, R = H, C_s, endo, exo). The hydrogen at C_{11} is bent 37° out of the $C_1C_{11}C_6$ plane.

4 (n = 3-6), as well as by the model calculations on $C_3H_5^+$,[6] the larger systems are more flexible and allow a greater degree of opening and a closer approach to the allyl-type structure. However, in all these "partially opened" species (4) the disrotatory twisting of the terminal allyl groups produces a strong bending of the hydrogen bound to the central carbon out of the plane defined by the three neighboring carbons.[6]

The MINDO/3 calculations have inherent limitations for systems of this type (cyclopropane strain energies are too low,[9] and the degree of ring opening in 4 (n = 3) has proceeded to a lesser extent than indicated by the ab initio results), but the expected trend of relative energies between the corresponding 3 and 4 isomers is given nicely (Table II; note the good agreement between the energy difference between 3 and 4 (n = 3) and that at the highest ab initio level). This trend corresponds to the observed relative solvolysis rates in the exo and endo series.[2]

The ^{13}C NMR spectrum of 5 (R = CH_3) shows the two six-membered rings to be unsymmetrical.[7] That this is due to the bending of the C_{11}-methyl group out of the $C_1C_6C_{11}$ plane is confirmed by MINDO/3 calculations, which show (Table II, Figure 2) the C_s conformations of 5 (R = H) to be about 15 kcal/mol lower than the cyclopropyl cation (C_{2v}) forms (with the C_{11}-hydrogen in the $C_1C_6C_{11}$ plane).

Acknowledgment. Dedicated to Prof. Dr. Ulrich Schöllkopf on the occasion of his 60th birthday. We thank the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the CONVEX Corporation for support, the last through assistance in purchase of a CONVEX C1 computer on which the calculations were carried out.

Registry No. 3 (n = 3), 36348-18-2; 3 (n = 4), 38892-84-1; 3 (n = 5), 113857-81-1; 5 (R = CH_3), 63734-87-2; 5 (R = H), 113892-34-5.

Synthetic Application of Photoinduced Single Electron Transfer Reactions: A Convenient Synthetic Approach for the 2,2-Dimethyl-2*H*-chromene System[1]

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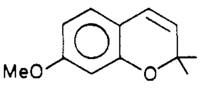
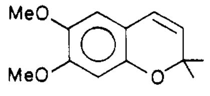
Ever since the visualization of precocene I and II (**1a** and **1b**) as antijuvenile hormone active compounds, isolated from *Ageratum houstonianum*,[2] several analogues of precocenes have been synthesized.[3] The 2,2-dimethyl-2*H*-benzopyran system has been noticed as parent molecule for all of these compounds.



1a



1b

Since these compounds represent the first insect endocrine antagonist to be discovered and appear to hold promise in the future development of insect control agents, a convenient synthetic approach is required. The synthetic procedures known so far are rather cumbersome and often end up in poor yields.[4]

We have reported[5] the photocyclization of substituted cinnamic acids to corresponding coumarins initiated by single electron transfer processes (Scheme I). In view of the mounting importance of the 2,2-dimethyl-2*H*-chromenes on the action of juvenile hormone antagonists, we herein extend the above observation for the synthesis of the 2,2-dimethyl-2*H*-chromene system.

Photolysis (>280 nm) of 3-aryl-1,1-dimethylprop-2-en-1-ol (**2a-f**), obtained by Grignard reaction of corresponding cinnamic acid esters, in the presence of 1,4-dicyanonaphthalene (DCN) generates an arene radical cation, which upon intramolecular nucleophilic attack by hydroxyl group on aromatic radical cation gave cyclized product (**3a-f**) as a single product in the identical manner as reported earlier.[5] The dissolved air present in the solvent system was enough to bring about the oxidation step. This reaction was also found to be slow in nitrogen atmosphere.[5,7] It must be noted here that most of the light was absorbed by **2a-f** under these experimental conditions. The chromenes **3a-f** were isolated by column chromatography and were characterized by IR, by ^1H NMR, and

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(1) RRL Communication No. 2072.

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