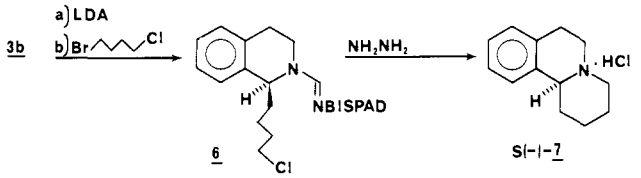
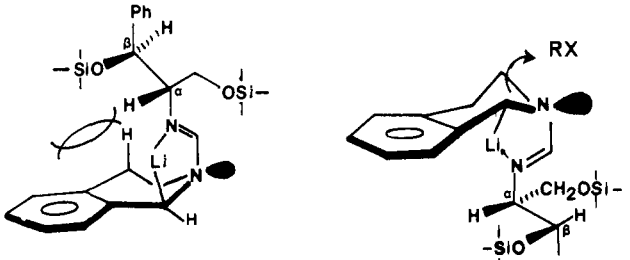
ployed in our laboratory for other asymmetric processes.[5] Silylation of the aminodiol with hexamethyldisilazane gave the bis-silylated phenylaminodiol (BISPAD).[6] The latter was treated with *N*-formyltetrahydroisoquinoline **2** to form the chiral formamidine **3b**.[6] Metalation of **3b** (LDA, -78 °C, THF) and addition



of various alkyl halides (-100 °C) furnished **4b**, which was heated in hydrazine-acetic acid, providing the 1-substituted tetrahydroisoquinolines **5** in good yields with enantiomeric excesses in excess of 90% for every case (Table I).[6] Furthermore, all five examples afforded the *S* configuration at C-1 of the isoquinoline. The effect of the temperature during the alkylation of **3b** can be seen in the table when methyl iodide was added at -78 °C giving the 1-methyl isoquinoline in 80% ee. Although not shown, the other alkyl halides also gave a 10-20% decrease in enantiomeric purity when added to the chiral lithio salt at -78 °C. This highly efficient enantioselective alkylation was further extended to provide the benzoquinolizine **7** in 90.3% ee by use of 1-bromo-4-chlorobutane as the electrophile. Thus, metalation of **3b** (-78 °C) followed by the addition of the dihalobutane (-100 °C) gave the chlorobutyl adduct **6**, which without purification was directly cyclized during hydrazinolysis[6] to (*S*)-hexahydrobenzoquinolizine in 70.3% yield (from **3b**); **7**·HCl: mp 260-262 °C, $[\alpha]_D^{24}$ -126.2° (*c* 0.42, EtOH).[7] In all cases the chiral BISPAD was recovered after hydrazine treatment and may be recycled for further use.

The high sense of chiral induction observed for the BISPAD auxiliary may presently be attributed to the conformational preference of the diastereomeric lithium salts D and E. In the



former, the enantiomeric BISPAD appears to lie over the plane of the isoquinoline ring whereas in E it is placed out and away from the isoquinoline due to the *S* configuration at the α-carbon. This conformational preference is much less apparent in the α-phenylethylamine (PEA) auxiliary, hence the lower alkylation selectivity. Furthermore, models indicate that the N-Cα bond is free to rotate, thus effectively blocking the bottom side of the E, which results in alkylation from the top side, giving the observed *S* configuration to the products. The configuration at the β-carbon may play a minor role since valinol trimethylsilyl ether or leucinol trimethylsilyl ether also give rather high enantioselective alkylation.[8] The main requirement appears to be a relatively bulky substituent at the β-carbon. Although the reaction has not yet been attempted, the enantiomeric BISPAD should favor D leading to the (*R*)-1-substituted tetrahydroisoquinolines, **5**. As alluded to earlier, the enantioselectivity is quite sensitive to the alkylation temperature, and if performed at -50 °C or higher, the products are formed in much lower enantiomeric excesses (0-30%). This is undoubtedly due to the difference in alkylation rates for D and E and their relative populations. Further studies on this interesting process are underway with a variety of prochiral amines.

Acknowledgment. We are grateful to the National Science Foundation for financial support. The award (to L.M.F.) of a postdoctoral fellowship by the National Institutes of Health is also acknowledged. We are indebted to Professor W. H. Pirkle for his assistance in the HPLC determinations of enantiomeric purity.

Supplementary Material Available: Experimental details and complete physical data for all compounds (6 pages). Ordering information is given on any current masthead page.

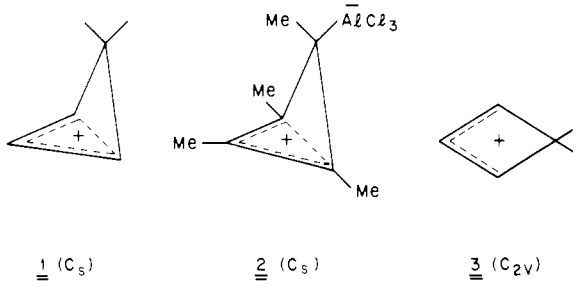
(5) Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 568.
(6) See supplementary material.
(7) mp 260-261 °C, $[\alpha]_D$ -140.0° (*c* 0.04, EtOH) for pure *S* enantiomer derived from degradation of virosecurinine (Craig, J. C.; Chan, R. P. K.; Roy, S. K. *Tetrahedron* **1967**, *23*, 3573).
(8) Use of valinol and leucinol trimethylsilyl ethers led to 1-substituted tetrahydroisoquinolines in 88-91% ee; however, the chemical yields are not yet satisfactory (Y. Kubota, research in progress).

Molecular Orbital Study of the Homocyclopropenylium Cation

R. C. Haddon* and Krishnan Raghavachari*

Bell Laboratories, Murray Hills, New Jersey 07974
Received September 2, 1982

The homocyclopropenylium cation (**1**; see also Figure 1) is the



simplest homoconjugated system[1] and the first species for which homoaromatic character was invoked.[2] It is also one of the best characterized homoaromatic compounds in a field where structural and thermodynamic information is difficult to obtain. Thus the structure of a derivative (**2**) is known,[3] and the barrier to ring inversion in **1** has been measured[4]—the activation energy for this latter process is usually considered to provide a measure of the energy difference between **1** and **3**, which has been termed the homoaromatization energy.[5] While qualitative theoretical arguments are successful in explaining the homoaromatic character of **1**,[6-8] quantitative calculations have given uneven results.[9] Semiempirical MO treatments (MINDO/2,[10] MINDO/3[8,11]) of **1** have enjoyed remarkable success, but ab initio Hartree-Fock (HF) calculations (STO-2G,[11,12] STO-3G,[12,13] 4-31G[12]) have failed

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Table I. Structures and Energies of the Homocyclopropenylium Cation

cation	method	bond lengths, Å			angles, deg		energies		ref
		1-2	1-3	1-4	α	β	total, hartrees	rel (1 → 3), kcal/mol	
1	MINDO/2	1.384	1.661	1.473	149.6				10
1	MINDO/3	1.402	1.739	1.502	149.3	8.7		9.8	8, 11, 12
3	MINDO/3	1.401	1.944	1.511	180	0			
1	HF/STO-2G	1.406	1.926	1.546	155.4	14.4	−147.76395	1.03	11, 12
3	HF/STO-2G	1.406	2.015	1.555	180	0	−147.76231		
1	HF/STO-3G	1.392	1.99	1.545	170.0	5.2	−152.20726	0.38	13
3	HF/STO-3G				180	0	−152.20665		
1	HF/STO-3G	1.392	1.920	1.539	156.6	12.9	−152.20844	0.72	*a, b, d*
3	HF/STO-3G	1.393	2.001	1.548	180	0	−152.20730		*a, c, e*
1	HF/4-31G	1.384	1.915	1.532	157.5	11.5	−153.79963	0.72	11, 12
3	HF/4-31G	1.385	1.993	1.540	180	0	−153.79848		
1	HF/6-31G	1.386	1.908	1.530	156.3	12.2	−153.96496	0.75	*a, b, f*
3	HF/6-31G	1.388	1.994	1.539	180	0	−153.96376		*a, c, g*
1	HF/6-31G*	1.373	1.787	1.507	148.1	17.7	−154.04251	4.36	*a, b, h*
3	HF/6-31G*	1.379	1.967	1.524	180	0	−154.03556		*a, c, i*
1	MP2/6-31G*	1.391	1.741	1.508	144.9	20.3	−154.52785	11.76	*a, b, j, l*
3	MP2/6-31G*	1.395	1.979	1.532	180	0	−154.50912		*a, c, k, l*
1	MP3/6-31G*			MP2/6-31G*			−154.55418	9.67	*m*
3	MP3/6-31G*						−154.53876		
1	MP4/6-31G*			MP2/6-31G*			−154.58158	9.73	*m, n*
3	MP4/6-31G*						−154.56608		
1	NMR							8.4 ± 0.5	4
2	X-ray	1.387	1.775	1.510	148.5				3

[a] Bond lengths (A-B), Å; bond angles (A-B-C), deg; dihedral angles (A-B-C-D), deg. [b] Geometrical parameters of 1 are in the order C-H1, C-H2, C-H4, C-H5, C2-C1-H1, X-C4-H4, X-C4-H5, X-C2-C1-H1. [c] Geometrical parameters of 3 are in the order C-H1, C-H2, C-H4, C2-C1-H1, X-C4-H4. [d] 1.102, 1.086, 1.092, 1.093, 131.8, 121.2, 127.0, 146.6. [e] 1.102, 1.084, 1.094, 133.7, 124.7. [f] 1.073, 1.065, 1.077, 1.078, 131.6, 121.3, 127.7, 147.2. [g] 1.073, 1.066, 1.080, 133.4, 125.2. [h] 1.077, 1.070, 1.077, 1.079, 129.4, 120.8, 126.2, 134.8. [i] 1.077, 1.071, 1.082, 133.1, 125.0. [j] 1.077, 1.070, 1.077, 1.079, 128.4, 119.6, 126.7, 129.0. [k] 1.077, 1.071, 1.082, 132.7, 124.9. [l] The C-H bond lengths were set to the HF/6-31G* values. [m] MP2/6-31G* geometry. HF/6-31G* energies: −154.04072 (1), −154.03500 (3) hartrees. Rel (1 → 3) 3.59 kcal/mol. [n] Full MP4 (see ref 17).

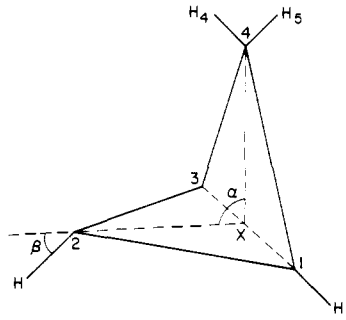

Figure 1. Labeling scheme for homocyclopropenylium cation structures **1–3**.

dismally in efforts to reproduce the experimental structure of **1** (assumed to be approximated by **2**[3]) and its barrier to ring inversion[4] (set to the calculated energy difference between **1** and **3**; Table I).

In the present study we have reexamined **1**, in the hope that it would be possible to achieve an improved correspondence between ab initio calculations and the available experimental results and also to establish the degree of sophistication that is required for the accurate calculation of the properties of homoaromatic systems in general.

The geometries and energies are collected in Table I, and it may be seen that the minimal (STO-2G, STO-3G)[14] and extended (4-31G, 6-31G)[15] basis set calculations give a similarly poor description of **1**. It is clear that these calculations underestimate the homoaromatic character of **1** from the long C1–C3 distance (>1.9 Å; cf. **2**), the flattened ring, and particularly the extremely small barrier to ring inversion (homoaromatization energy).

The inclusion of polarization functions on carbon (6-31G*)[16] greatly improves the calculated geometry of **1**, and it is apparent that the exigencies of the bonding situation in **1** require a particularly flexible basis set; it is tempting to suggest that this originates from the movement of π-type basis functions into the C1–C3 region of homoconjugation, which is facilitated by the presence of carbon polarization functions (the population analysis supports this interpretation). The most dramatic effect occurs upon inclusion of electron correlation [at the level of second-order Moller–Plessett theory[17] (MP2)] in the calculations (Table I), and the strength of the homoconjugate interaction is somewhat overestimated at this level. The third-order term (MP3) corrects most of this discrepancy and, bearing in mind the zero point correction which would slightly decrease the calculated barrier, rationalizes the theoretical and experimental estimates for the barrier to ring inversion in **1**. The calculated energy difference remains unchanged on inclusion of the fourth-order term (MP4). The calculated structure of **1** is also in substantial agreement with that observed for **2**; given the finding[4] that methyl substitution decreases homoconjugation in **1**, the correspondence between the results on **1** and **2** is only expected to be approximate.

The effect of electron correlation in stabilizing **1** at the expense of **3** (to the extent of 5.4 kcal/mol at the MP4 level) is in line with our previous studies, which have shown that the inclusion of electron correlation favors delocalized aromatic systems over localized nonaromatic structures.[18] The present system is unique in that electron correlation favors the structure with the larger energy gap (14.52 eV (**1**) and 12.09 eV (**3**), HF/6-31G*). The behavior of the energy gap is in accord with the HMO picture of this system,[19] which ascribes to **1** an energy gap intermediate

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between the cyclopropenylium cation (3.0β) and the allyl cation (1.4β; approximated by **3**).

The results of this study are remarkable in that they suggest that highly sophisticated theoretical techniques are required to satisfactorily address problems pertaining to homoaromatic character.

π Complexing of Chlorine Atoms: Is That All There Is?

Philip S. Skell,* Harry N. Baxter, III, and Charles K. Taylor

Department of Chemistry, The Pennsylvania State University University Park, Pennsylvania 16802

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Russell[1] and Walling and Mayahi[2] described the effect of solvation on the selectivity of chlorine atoms in hydrogen abstraction reactions. Aromatic solvents and carbon disulfide were found to be especially effective in moderating the H-abstracting reactions of chlorine atoms. This effect was rationalized with the concept of π complexation of the chlorine atom. While this rationalization was sufficient to explain most of the observations, there were some aspects that were not so felicitously consistent, and this led us to an exploration of an experimental region not encompassed in the original work.

The earlier studies used substrates at high concentrations, typically 1-3 M. With low concentration of substrates the H-abstracting species would live longer before encountering a substrate molecule. The π-complex rationalization would predict no change in selectivity with decreasing concentration of substrate, only, perhaps, a decrease in yield of chlorinated substrate. We report here that *a very marked increase of selectivity occurs with progressive diminution of the substrate concentration.*

The experimental design was essentially the same as in the earlier reports. Dilute Cl_2 in argon was bubbled through the deoxygenated reaction solutions while irradiating with a tungsten lamp. Conversions of substrate were kept low by limiting the amount of Cl_2 to preclude polychlorination, typically 5-15% conversions of alkane substrate. The substrate was 2,3-dimethylbutane, and the yields of primary and tertiary halides were determined by gas chromatography. We report here the tertiary to primary ratio on a per hydrogen basis (S).

Table I gives S as a function of alkane concentration in 4.0 M benzene solvent. At the highest concentrations of alkane these results are similar to those in the earlier reports; at low concentrations the selectivities are much higher. Since there is no change in the benzene concentration in this series of experiments, the π-complexation equilibrium cannot be affected.

$$Cl\cdot + \text{arene} \rightleftharpoons (\text{arene}\cdot Cl)$$

All indications point to rapid establishment of equilibrium between free chlorine atom and the π complex—particularly in media where the arene is the solvent. Alteration of alkane concentration should not affect selectivity if the above species are the only two abstractors. The only effect of a 100-fold reduction of alkane concentration would be a corresponding increase in the average time required for an encounter between a chlorine atom and an alkane molecule: with 1 M alkane, $\sim 10^{-10}$ s, with 0.01 M alkane, $\sim 10^{-8}$ s. However, within this time frame, provided by using low alkane concentrations, it is apparent that the concentration of a more selective H abstractor is increasing.

Analogous occurrences have been observed in 4.0 M CS_2 in CCl_3F (Table II). In CCl_3F, as reported earlier,[1,2] there is no solvent effect: at all concentrations of alkane we find the tertiary to primary selectivity to be 4.15 ± 0.1, characteristic of a free chlorine atom chain.

Table I. Photochlorination of 2,3-Dimethylbutane in 4 M Benzene at 20 °C (CCl_3F as Diluent)

$[(CH_3)_2CHCH(CH_3)_2]^a$	S(3°/1°)
4.7	16.1
1.0	33.2
0.51	37.5
0.20	50.2
0.10	52.8
0.050	53.6
0.020	56.0

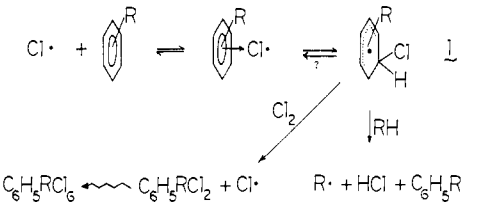
[a] mol L^{-1}.

Table II. Photochlorination of 2,3-Dimethylbutane in 4.0 M Carbon Disulfide at 13 °C (CCl_3F as Diluent)

$[(CH_3)_2CHCH(CH_3)_2]^a$	S (3°/1°)
5.8	22
2.0	34
1.0	51
0.51	60
0.25	73
0.11	93
0.051	107

[a] Mol L^{-1}.

Scheme I



The effect of Cl_2 concentration was examined by carrying out two sets of experiments in chlorobenzene. In the first set, the 2,3-dimethylbutane concentration was 2.0 M, and all conditions, except for the manner of Cl_2 introduction, were identical. In one experiment, chlorine was introduced over a 20-min period with steady illumination as described above. Under these conditions the color of chlorine was not evident, indicating a Cl_2 concentration <0.03 M. In the other experiment, the same amount of chlorine was added in the dark ($[Cl_2]_i \sim 0.1$ M) and then illuminated. The observed selectivities were 18.2 and 19.5, respectively.

In the second set of experiments, the 2,3-dimethylbutane concentration was 0.20 M in 4.0 M benzene (CCl_3F diluent). With initial chlorine concentrations 0.02 M the selectivity is 50.2; with 0.01 M Cl_2 the selectivity is 52.4. In the second, the chlorine was admitted as in the first, but the distance from the light source was 5 times greater. In the third experiment, the chlorine was introduced in the dark ($[Cl_2]_i \sim 0.07$ M) and subsequently illuminated at the same close range as in the first experiment. The selectivities were 96, 88, and 91, respectively; within experimental error, these are the same.

Although earlier studies had demonstrated that interconversions of alkyl radicals (e.g., 1° → 3°) do not occur in chlorinations of alkanes, it was deemed advisable to examine this possibility under our reaction conditions. In no instance was there any indication such rearrangements were occurring. Experiments were run at 0.08 M 2,3-dimethylbutane in CCl_3F, with chlorine concentrations of <0.03 M, and $[Cl_2]_i = 0.07$ and 0.50 M (the excess chlorine was removed with the argon after brief illumination). The observed selectivities were 4.1, 4.2, and 4.8, respectively. Within the time frame permitted by 0.03 M chlorine concentrations, no interconversion of the alkyl radicals is indicated.

A limited examination of the effect of temperature on selectivity was carried out for the 4.0 M CS_2 system (CCl_3F solvent) between 15 and -96 °C. With 5.8 M alkane, temperature has no effect on S. At 0.25 M alkane, the observed selectivity increases sharply with decreasing temperature.

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