Tetrahedron Letters, Vol. 34, No. 1, pp. 99-102, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

Stabilization of the 1-Naphthyltropylium Ion by [2.2]Paracyclophane Fixed at the Face-to-Face Position to the Tropylium Ring

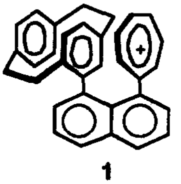
Koichi Komatsu,* Ryotaro Tsuji, Yoichiro Inoue, and Ken'ichi Takeuchi

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

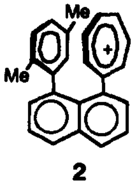
Key Words: tropylium ion; [2.2]paracyclophane; charge-transfer interaction; pK_{R^+}; AM1 calculation

Abstract: *The title cation, in which [2.2]paracyclophane and the tropylium ring are rigidly fixed at the face-to-face arrangement, was synthesized, and was found to exhibit the highest stability in a series of (8-substituted 1-naphthyl)tropylium ions prepared so far.*

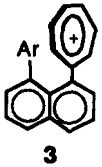
A typical textbook description for the mode of carbocation stabilization is the inductive and conjugative electron donation from the substituents. The through-space π-electron supply from a π-donor closely placed in the same molecule can also be regarded as another mode of carbocation stabilization, which may be recognized as the intramolecular charge-transfer interaction.[1] On the other hand, [2.2]paracyclophane is known to have the π-cloud highly expanded outside of the molecule due to the enforced stacking of the two benzene rings.[2] Then it is of particular interest to examine how such a π-system can electronically stabilize a carbocation fixed closely in the same molecule. From such viewpoint, we have prepared the title cation **1** with the tropylium ring directly facing to the cyclophane group, together with the reference cation **2**, and compared their properties with those of the previously reported cations **3**.[3]



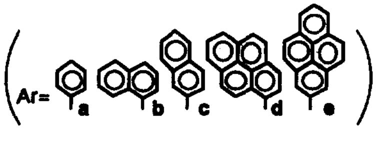
1



2

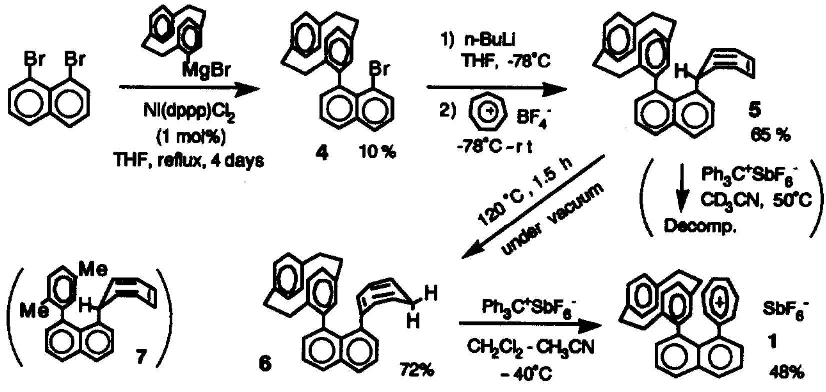


3



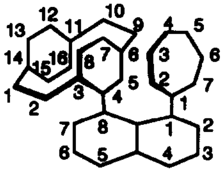
The synthetic route is shown in Scheme 1. Grignard coupling of 1,8-dibromonaphthalene with [2.2]paracyclophan-4-ylmagnesium bromide was quite sluggish, but afforded the product **4**[4] in 10 % yield after heating for 4 days under the catalysis with dichloro[1,3-bis(diphenylphosphino)propane]nickel ($Ni(dppp)Cl_2$). The bromide **4**, isolated by medium pressure liquid chromatography, was converted to the cycloheptatriene **5**.[5] The direct conversion of **5** to **1** was not successful, but the thermal [1,5]sigmatropy of **5** to its isomer **6** took place readily at 120 °C as compared with the case of the reference compound **7**,[6] which required heating at ~170 °C for 1.5 h for completion.[7] The hydride abstraction with $Ph_3C^+SbF_6^-$ at –40°C afforded the SbF_6^- salt of the desired cation **1**[8] as a dark-red powder after precipitation with ether. The SbF_6^- salt of the cation **2**[9] was prepared as an orange powder in the same way.

Scheme 1



The ^1H and ^{13}C NMR data of the cation **1** are shown in Table 1. The assignments were made based on the H/H and C/H COSY 2D-NMR technique. It is to be noted that the tropylium ring protons exhibit the sequential upfield shift in circulating order around the ring and correspondingly the H-8 signal of the cyclophane ring is upfield shifted to δ 5.47. These data indicate that the conformation of the tropylium ring is fixed so that half of the ring is heavily shielded by the closely positioned cyclophane's benzene ring.

Table 1. ^1H (270 MHz) and ^{13}C NMR (67.8 MHz) Data (δ) for the Cation $1 \cdot SbF_6^-$ in CD_2Cl_2

(position)	^1H	^{13}C	(position)	^1H	^{13}C	(position)	^1H	^{13}C
Tropylium			Cyclophane, Aromatic [a]			**Naphthalene** [a]		
(1)	——	171.2	(5)	6.70	132.2	(2)	7.68	136.7
(2)	9.09	148.1	(7)	6.31	135.7	(3)	7.80	126.1
(3)	8.73	151.0	(8)	5.47	137.4	(4)	8.31	134.5
(4)	8.57	149.1	(12)	6.57	132.4	(5)	8.24	130.4
(5)	8.42	151.8	(13)	6.57	132.5	(6)	8.01	127.9
(6)	7.65	146.3	(15)	6.41	133.4	(7)	8.06	132.4
(7)	7.57	151.5	(16)	6.56	128.9	**Numbering system** =		
			Cyclophane, Aliphatic					
			(1)	2.58, 2.42	34.7			
			(2)	2.17, 2.03	33.7			
			(9)	3.10	35.4			
			(10)	3.10	35.4			

[a] δ (^{13}C) for quaternary carbons: 143.2, 141.9, 140.6, 140.3, 140.0, 138.0, 137.3, 135.7, 129.8.

Semi-empirical molecular orbital (MO) calculations (AM1) indicated the optimized structure of **1** to be as shown in Fig. 1.[10] The results suggest that the three aromatic rings are arrayed in a face-to-face arrangement in close proximity and the tropylium and benzene rings are mutually half-overlapped in good agreement with the ^1H NMR data. The distance between the centers of tropylium and the facing benzene rings is calculated to be 3.4 Å. In this structure (the conformer A in Fig. 2), the tropylium and cyclophane rings are twisted with reference to the naphthalene plane by 49.8° and 60.5° respectively, so that the close contact is avoided between the naphthalene's H-7 and the methylene protons at the C-1 (and C-2) of the cyclophane's ethano-bridge. Another conformer (**B**) in which both of the aromatic substituents are twisted in an opposite direction, would involve steric congestion at the naphthalene's H-7 proton and is calculated to be 1.1 kcal/mol less stable than the conformer A by AM1.

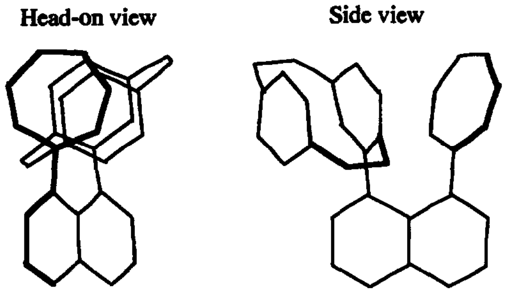


Fig. 1. The calculated structure of **1** by AM1.

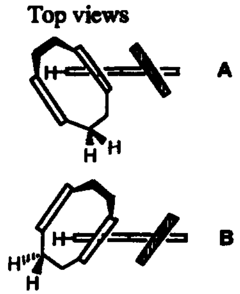


Fig. 2. Schematic representations for conformers **A** and **B**.

The cations **1** and **2** exhibited the longest-wavelength absorption in dichloromethane at 555 and 500 nm, respectively. The transition energy of these absorptions are linearly correlated with the ionization potential (IP) of the donor molecules, including the previously reported cations **3a**-**e** (correlation coefficient, 0.986; slope, 0.70), supporting the assignment of these absorptions as the intramolecular charge-transfer bands.

The data of pK_{R^+} and reduction potential, together with $h\nu_{CT}$, for the cations **1**, **2**, and **3a**-**e** are shown in Table 2 in a decreasing order of the $h\nu_{CT}$ value. Also shown are the values for the energy gap, $\Delta E_{H\text{-}L}$ (calculated by AM1), between the HOMO and LUMO which are localized at the donor and acceptor moieties respectively. The $\Delta E_{H\text{-}L}$ values exhibit, again, a good correlation with the observed $h\nu_{CT}$ values (correlation coefficient, 0.990; slope, 0.61).

Table 2. Data of $h\nu_{CT}$, $\Delta E_{H\text{-}L}$, pK_{R^+}, and Reduction Potential (E_{red}) for the Cations **1**, **2**, and **3a**-**e**

Cation	donor's IP / eV	$h\nu_{CT}$ ^{a} / eV	$\Delta E_{H\text{-}L}$ / eV	pK_{R^+} ^{b}	E_{red} ^{c} / V vs Ag/Ag$^+$
3a	9.23	3.16	6.78	5.03	−0.597
2	8.44	2.48	5.84	5.37	−0.627
3b	8.26	2.43	5.68	6.27	−0.649
3c	8.26	2.36	5.62	5.45	−0.601
1	8.08	2.23	5.39	6.30	−0.689
3d	7.72	2.12	5.03	6.28	−0.665
3e	7.72	2.07	5.03	5.75	−0.625

[a] Obtained from the charge-transfer absorption in CH_2Cl_2. [b] Determined spectrophotometrically in 50% aq. CH_3CN. [c] Cathodic peak potential obtained by cyclic voltammetry in CH_3CN with $(C_4H_9)_4NClO_4$ as a supporting electrolyte: scan rate, 0.1 V/s.

The data of both the pK_{R^+} and reduction potential indicate that the cation **1** is thermodynamically stabilized to the same extent as the cation **3d** having a condensed aromatic π-system, pyrene, as a π-donor. The pK_{R^+} value of **1** is nearly 1 unit increased as compared with the reference cation **2**.[11] This stabilization is apparently attributed to the π-electron donation from the stacked π-system of the [2.2]paracyclophane moiety. The total electron density residing in the donor and acceptor moieties was calculated by the semi-empirical MO (INDO) method and is shown in Fig. 3. It implies that the cyclophane system does electronically stabilize the tropylium ion by the through-space π-electron supply which appears to induce the ion-dipole interaction in the stacked π-systems.

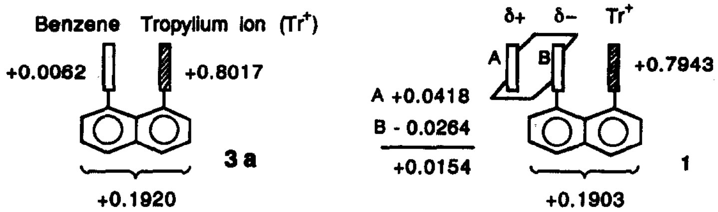


Fig. 3. The total electron densities calculated by INDO MO method.

Acknowledgment: We are indebted to Professor Armin de Meijere of Georg-August-University of Göttingen, who has first suggested us the possible unique properties of the cation **1**.

REFERENCES AND NOTES

1. For examples having the tropylium ions, see the literatures cited in ref. 3.
2. D. J. Cram and J. M. Cram, *Acc. Chem. Res.* **1971**, *4*, 204, and the literatures cited therein.
3. R. Tsuji, K. Komatsu, Y. Inoue, and K. Takeuchi, *J. Org. Chem.* **1992**, *57*, 636.
4. **4**; mp 211-212 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.92 (d, 1H), 7.91 (d, 1H), 7.88 (d, 1H), 7.72 (dd, 1H), 7.70 (d, 1H), 7.25 (dd, 1H), 6.73 (d, 1H), 6.68 (s, 1H), 6.67 (d, 1H), 6.60 (d, 1H), 6.58 (d, 1H), 6.54 (d, 1H), 6.44 (d, 1H), 3.29-2.99 (m, 5H), 2.67 (dd, 1H), 2.47 (dd, 1H), 2.08 (dd, 1H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 140.5 (s), 140.0 (s), 139.7 (s), 139.6 (s), 139.0 (s), 138.9 (s), 135.9 (s), 135.1 (d), 133.7 (d), 133.1 (d), 133.1 (d), 132.5 (d), 131.8 (d), 131.3 (d), 131.0 (d), 129.0 (d), 128.6 (d), 128.6 (d), 128.3 (s), 125.8 (d), 125.5 (d), 119.8 (s), 35.5 (t), 35.4 (t), 34.9 (t), 32.8 (t).
5. **5**; mp 71-72 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.91 (d, 1H), 7.83 (d, 1H), 7.71 (d, 1H), 7.64 (d, 1H), 7.63 (dd, 1H), 7.53 (dd, 1H), 6.66 (d, 1H), 6.56 (d, 1H), 6.55 (s, 1H), 6.51 (d, 1H), 6.47 (d, 1H), 6.36 (d, 1H), 6.19-6.08 (m, 3H), 5.94 (dd, 1H), 5.70 (dd, 1H), 5.32 (dd, 1H), 4.71 (dd, 1H), 3.18-2.86 (m, 4H), 2.63-2.29 (m, 4H), 2.11-1.99 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 144.1 (s), 140.9 (s), 140.0 (s), 139.4 (s), 138.9 (s), 138.7 (s), 138.0 (s), 136.7 (d), 134.8 (s), 132.8 (d), 132.3 (d), 132.2 (s), 132.1 (d), 131.8 (d), 130.6 (d), 130.4 (d), 129.9 (d), 129.8 (d), 128.9 (d), 128.7 (d), 128.7 (d), 128.5 (d), 128.5 (d), 127.4 (d), 125.6 (d), 124.6 (d), 124.1 (d), 123.0 (d), 43.5 (d), 35.4 (t), 35.4 (t), 34.9 (t), 33.4 (t).
6. **7** (prepared in the same way as **5**); mp 82-83 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.84 (d, 2H), 7.69 (d, 1H), 7.51 (dd, 1H), 7.41 (dd, 1H), 7.13 (d, 1H), 6.96 (d, 1H), 6.90 (d, 1H), 6.88 (s, 1H), 6.24 (dd, 2H), 5.92 (m, 2H), 5.26 (dd, 1H), 5.01 (dd, 1H), 2.97 (dd, 1H), 2.21 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 143.7 (s), 143.2 (s), 138.7 (s), 135.0 (s), 134.5 (s), 132.2 (s), 130.9 (s), 130.0 (d), 129.7 (d), 129.7 (d), 129.6 (d), 129.2 (d), 129.0 (d), 128.9 (d), 128.8 (d), 128.0 (d), 127.7 (d), 127.4 (d), 125.6 (d), 124.5 (d), 123.6 (d), 123.0 (d), 41.8 (d), 20.8 (q), 19.8 (q); Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88 %. Found: C, 92.96; H, 6.90 %.
7. This would be ascribed to the greater release of steric strain upon thermal isomerization for **5** than for **7**.
8. $1\cdot SbF_6^-$; mp 158-159 °C (dec); UV-vis (CH_2Cl_2) λ_{max} 272 nm (log ε 4.13), 308 (3.94), 388 sh (3.72), 447 (3.89), 555 sh (3.29); UV-vis (CH_3CN) λ_{max} 264 nm (log ε 4.08), 303 (3.96), 421 (3.86); Anal. Calcd for $C_{33}H_{27}F_6Sb$: C, 60.12; H, 4.13%. Found: C, 59.49; H, 4.19%.
9. $2\cdot SbF_6^-$; mp 190-191 °C (dec); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 8.70 (d, 1H), 8.68-8.52 (m, 3H), 8.41 (m, 2H), 8.24 (d, 1H), 8.12 (d, 1H), 7.75 (dd, 1H), 7.72 (dd, 1H), 7.52 (d, 1H), 7.51 (d, 1H), 6.79 (s, 1H), 6.68 (d, 1H), 6.54 (d, 1H), 2.16 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 170.9 (s), 153.7 (d), 151.5 (d), 151.2 (d), 150.3 (d), 150.2 (d), 148.4 (d), 142.4 (s), 137.6 (s), 137.6 (s), 137.3 (s), 135.6 (s), 135.4 (d), 134.2 (d), 133.7 (s), 132.9 (d), 132.1 (d), 132.1 (d), 130.3 (d), 130.1 (d), 128.9 (s), 127.5 (d), 125.9 (d), 20.8 (q), 19.7 (q); UV-vis (CH_2Cl_2) λ_{max} 277 nm (log ε 4.09), 368 (3.72), 413 (3.72), 500 (3.57); UV-vis (CH_3CN) λ_{max} 274 nm (log ε 4.09), 350 (3.70), 394 (3.72), 470 sh (3.53); Anal. Calcd for $C_{25}H_{21}F_6Sb$: C, 53.89; H, 3.80 %. Found: C, 53.60; H, 3.91 %.
10. Results of MMP2 calculations also gave a quite similar structure.
11. The energy difference in the covalent structures is assumed to be not so large as to affect the pK_R^+ difference, since the nucleophilic attack of OH^- should occur preferentially at the tropylium ring carbons far from the ipso-carbon.

(Received in Japan 18 August 1992)