

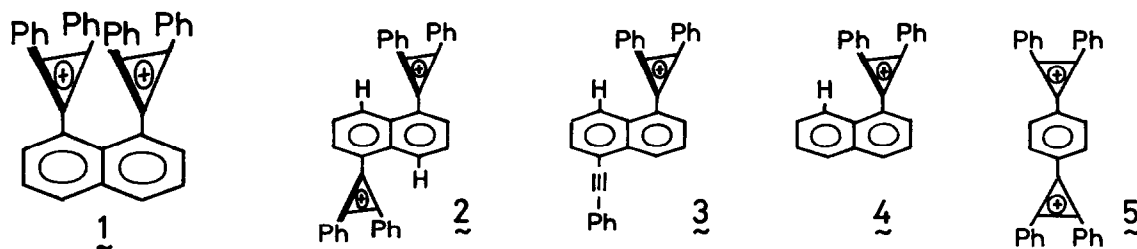
SYNTHESIS, PROPERTIES, AND REDUCTION OF
 1,8-NAPHTHYLENEBIS(DIPHENYLCYCLOPROPENIUM) DICATION ¹⁾

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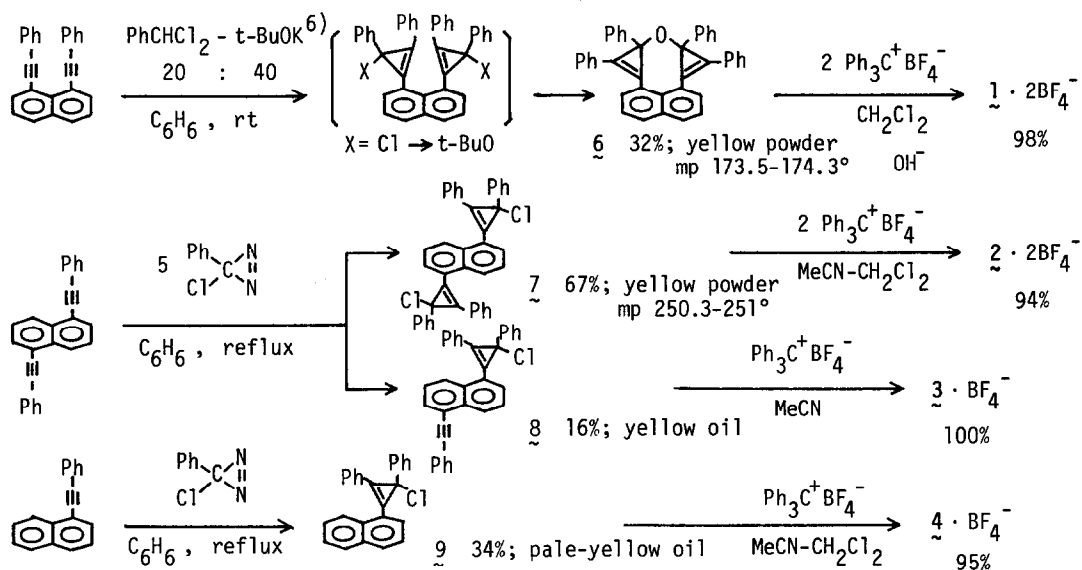
Abstract: Synthesis, properties, and the result of one-electron reduction are described for the title compound, which is the first example of the stable dication containing two cationic rings in a close face-to-face arrangement.

Various types of carbocyclic compounds containing intramolecularly interacting π -systems have been subjected to both synthetic and theoretical studies. Especially those having a nonbenzenoid aromatic cation as a strong π -acceptor are of current interest because of their novel property as a new type of intramolecular CT complexes.²⁾ As a matter of course, attempts have also been made to synthesize the dicationic analogs which have two positively charged π -systems fixed in close proximity, but such species have not allowed isolation nor spectral investigation due to the extreme instability inevitably present in such systems.³⁾ In this paper we wish to report on the synthesis of the title compound (**1**) as the first example of the stable dication with two positive rings fixed in a face-to-face conformation at close location. The properties will be discussed with reference to the dication **2** having the two cationic rings at remote positions, the structurally related monocations **3** and **4**, and the *p*-phenylenebis-(diphenylcyclopropenium) dication (**5**) reported by Eicher and Berneth.⁴⁾



The syntheses utilized the addition of phenylchlorocarbene to respective acetylenic compounds as shown in Scheme 1. The intramolecular dicyclopropenyl ether **6**,⁵⁾ which was formed by succeeding reactions, was isolated by the use of PTLC (C_6H_6 - n - C_6H_{14} (2:1)/ SiO_2) followed by recrystallization from $CHCl_3$ - n - C_6H_{14} , while the covalent chlorocyclopropenes, **7**, **8**, and **9** were isolated by crystallization from CH_2Cl_2 -MeCN, preparative HPLC (C_6H_{14} /microporasil), and PTLC (C_6H_6/SiO_2), respectively; then, the cyclopropenes were converted quantitatively into the corresponding cation salts by treatment with $Ph_3C^+BF_4^-$.

Scheme 1

Table 1. Physical and Spectral Properties of the Tetrafluoroborates of 1, 2, 3, and 4^a

Compd	IR ν (KBr) cm^{-1}	UV λ_{max} nm (log ϵ)	^1H NMR (220 MHz) δ (CD_3CN) ppm		^{13}C NMR δ (CD_3CN) ppm		
			Ph	Naph	∇	Ph	Naph
$1 \cdot 2\text{BF}_4^-$	1410 vs 1060 b, vs	244 (4.55) 303 (4.67) 377 (4.33) 393 (4.31)	8.04 (o) 7.76 (p) 7.63 (m)	9.03 (H-2) 8.97 (H-4) 8.31 (H-3)	154.5 ^b 154.0 ^c	139.6 (p) 136.4 (m) 131.1 (o) 119.0 (i)	141.5 (C-2) 140.5 (C-4) 135.4 (C-4a) 131.7 (C-8a) 129.2 (C-3) 129.0 (C-1)
$2 \cdot 2\text{BF}_4^-$	1415 vs 1060 b, vs	240 (4.62) 261 (4.60) 286 (4.62) 301 (4.64) 365 (4.55) 383 (4.54)	8.59 (o) 8.08 (p) 7.95 (m)	8.97 (H-2) 8.73 (H-4) 8.24 (H-3) (100 MHz)	159.0 ^b 155.3 ^c	140.1 (p) 137.1 (m) 131.7 (o) 121.1 (i)	138.1 (C-2) 135.2 (C-4) 132.9 (C-4a) 130.5 (C-3) 121.2 (C-1)
$3 \cdot \text{BF}_4^-$	2220 w 1395 vs 1055 b, vs	230 (4.56) 254 (4.49) 297 (4.61) 392 (4.21)	8.54 (o) 8.2–7.9 (m, p) 7.8–7.4 (=Ph) (100 MHz)	9.11 (H-4) 8.80 (H-2) 8.2–7.9 (H-3, 6~8)	157.9 ^b 155.3 ^c	139.6 (p) 136.9 (m) 131.6 (o) 121.2 (i)	137.8 133.2 130.4 128.0 126.5 123.8 119.6
$4 \cdot \text{BF}_4^-$	1420 vs 1060 b, vs	213 (4.79) 261 (4.38) 285 (4.42) 338sh (4.20) 361 (4.27)	8.53 (o) 8.07 (p) 7.90 (m)	8.78 (H-2) 8.60 (H-4) 8.2–7.8 (H-3, 5~8)	157.8 ^b 155.4 ^c	139.4 (p) 136.8 (m) 131.5 (o) 121.3 (i)	140.1 137.8 132.6 131.0 130.9 129.2 127.0 125.9 119.0

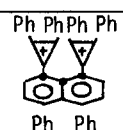
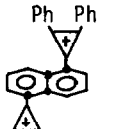
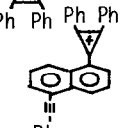
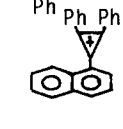
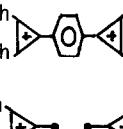
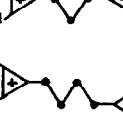
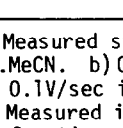
a) All the salts gave satisfactory elemental analyses. b) $\text{Ph} \nabla \text{Ph}$ c) $\text{Naph} \nabla \text{Naph}$

All of the new tetrafluoroborate salts of 1-4 are stable under air, and exhibit the properties listed in Table 1. Noteworthy is the apparent upfield shift of the ^1H NMR signals of phenyl protons in 1 as compared with those in 2 ($\Delta\delta$ 0.55 (*o*), 0.32 (*m*), and 0.32 (*p*) ppm), clearly demonstrating the ring current effect of the facing benzene ring and thereby the face-to-face conformation of two diphenylcyclopropenium rings in 1.⁷⁾ The similar upfield shift is also noted for the ^{13}C NMR signals of the cyclopropenium carbons in 1, while the downfield shift is observed for the naphthalene ring carbons (especially C-2, 4, 4a, and 1). In ^{13}C NMR spectra of rigid molecules containing crowded π -systems, the ring current effect is known to be obscured by the dominating π - π compression effect.⁸⁾ Therefore, in the present case, the small but appreciable shielding and deshielding observed respectively for the cyclopropenium and naphthalene carbons should rather be ascribed to a change in charge densities due to slight "leaking out" of the dipositive charge, which was locally accumulated at closely placed two three-membered rings, inductively into the neutral naphthalene ring through the σ -framework.

It may well be anticipated, then, that the presence of two cationic rings at such close proximity should result in considerable destabilization of the dicationic system as a whole. Actually, the results of pK_R^+ measurements given in Table 2 reveal that the marked destabilization is brought about by introduction of the second cyclopropenium ring at the 8-position (as in the dication 1) as compared with that at the 5-position (as in the dication 2). The pK_R^+ difference between 1 and 2, which amounts to -1.66, is ascribed to the destabilization due to the electrostatic repulsion of the cationic rings closely facing each other. Since a comparable amount of pK_R^+ difference (-1.32) is observed between the trimethylene- (10) and tetramethylene-dications (11),⁹⁾ it is supposed that most of the destabilization in 1 is caused by the electronic interaction of the two cationic rings through the σ -bond of the naphthalene framework and the effect of the through-space interaction is relatively small.

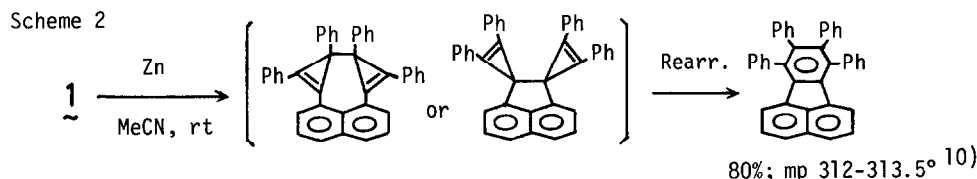
On the other hand, the dication 2 is less destabilized than the *p*-phenylene-type dication 5,⁴⁾ reflecting less π -conjugative interaction between the two positive rings across the 1,5-naphthylene system.

Table 2. pK_R^+ and Reduction Potentials

Cation	pK_R^+ ^a	$E_\text{Red'n}$ ^b V vs Ag/Ag ⁺
	(<u>1</u>) -2.08 ^c (1.11) ^d	-0.54
	(<u>2</u>) -0.42 ^c (1.78) ^d	-0.75
	(<u>3</u>) 1.16	-1.04
	(<u>4</u>) 1.62	-1.07
	(<u>5</u>) ^e -1.1 ^{c,e} (3.5) ^d	-0.32 ^e (in DMF)
	(<u>10</u>) ^f 2.06 (4.50) ^d	-0.95
	(<u>11</u>) ^f 3.38 (4.75) ^d	-1.16

a) Measured spectrophotometrically in 50%-aq.MeCN. b) CV peak potential at scan rate of 0.1V/sec in MeCN with TBAP (0.1M). c) Measured in dil.H₂SO₄-EtOH by the use of Co^0 function calibrated with (*p*-MeOC₆H₄)₂PhC⁺ according to N.C.Deno et al., *J. Am. Chem. Soc.*, 83, 2367 (1961). d) Value for the second neutralization. e) Ref. 4. f) Ref. 9.

The values of reduction potential also given in Table 2 exhibit the general trend similar to that for pK_R^+ values, indicating the greatest susceptibility of **1** towards one-electron reduction. Thus, the chemical reduction of **1** with excessive zinc powder smoothly afforded 7,8,9,10-tetraphenylfluoranthene¹⁰) as a single product, most probably by way of the initial formation of 1,8-naphthylenebis(diphenylcyclopropenyl), the intramolecular coupling product of 1,8-naphthylenebis(diphenylcyclopropenyl) diradical, as shown in Scheme 2. The subsequent bicyclopropenyl→benzene rearrangement may involve a highly strained Dewar benzene or benzvalene as an intermediate according to the recent mechanistic studies.¹¹⁾



References and Notes:

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- 5) Also formed by complete neutralization of **1**: IR ν (KBr) 1800(m), 1125(m), 1100(m) cm^{-1} , UV λ_{max} (MeCN) 230 nm (log ϵ , 4.64), 247 (4.61), 314 (4.38), 328 (4.38), 350 (4.26); ^1H NMR (220 MHz) δ (CDCl_3) 8.26 (d, 2H, Naph-H-2), 7.91 (d, 2H, Naph-H-4), 7.87 (d, 4H, o-H), 7.60 (t, 2H, Naph-H-3), 7.46 (m, 6H, m,p-H), 7.17 (d, 4H, o-H'), 6.97 (m, 6H, m,p-H'); ^{13}C NMR δ (CDCl_3) 144.1-124.2 (14 peaks, Ar-C), 119.2 ($\text{C}_{10}^{\text{Ph}}$), 117.9 ($\text{C}_{9}^{\text{Naph}}$), 65.8 ($\text{C}_{10}^{\text{Ph}}$); Anal. Calcd for $\text{C}_{40}\text{H}_{26}$: C, 91.92; H, 5.01%. Found: C, 91.52; H, 5.07%.
- 6) This method is similar to the one used for the synthesis of **5** (Ref. 4). The use of phenylchlorodiazirine as the carbene generator was found unsuitable because of the instability of the first formed mono-carbene-adduct under the reaction conditions leading to a complex mixture of byproducts.
- 7) A comparable amount of upfield shift ($\Delta\delta$ 0.53) is observed for the facing phenyl protons in 1,8-diphenylaphthalene: H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).
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