

Tripolar Mesoionic Compounds

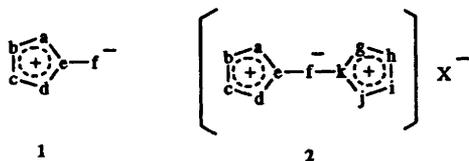
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Tripolar mesoionic compounds have been synthesized by the reaction of (1,3-diphenyltetrazol-5-ylidene)cyclopentadienide (or -indenide) with the dicationic ether salts derived from mesoionic olates and trifluoromethanesulfonic anhydride. The structures of the newly prepared mesoionic systems are discussed on the basis of spectroscopic analysis; it is shown that the tripolar [tetrazolium–cyclopentadienide (or indenide)–tetrazolium] canonical structure contributes significantly to the ground state of these compounds.

Introduction

Mesoionic compounds have received much attention and have been extensively studied because of their unique structures, reaction behaviour, and pharmaceutical activities.¹ Mesoions can be expressed by the general formula **1** where a–f represent suitably substituted carbons or heteroatoms. The mesoionic compounds hitherto prepared bear a chalcogen atom (O, S, and Se), an imino group (NR), or a carbanionoid group (CRR') as the anionic exocyclic group (f). When two mesoionic molecules share a common exocyclic group (f), a new type of cationic system of the tripolar formula **2** is produced; however, such tripolar mesoionic systems are rarely studied. We described here the synthesis and properties of this type of mesoionic compound, in which two heterocyclic five-membered rings are linked by a cyclopentadienide or an indenide ring.



Results and discussion

Synthesis

(1,3-Diphenyltetrazol-5-ylidene)cyclopentadienide **3**² was added to a suspension of bis(1,3-diphenyltetrazolium) ether di(trifluoromethanesulfonate) (ditriflate) **4**, prepared from the reaction of 1,3-diphenyltetrazolium-5-olate and triflic anhydride.³ The reaction proceeded smoothly to give a dark orange solution. Purification by column chromatography gave a 3:2 mixture of isomeric mesoionic compounds **5** and **6** in 53% combined yield (Scheme 1). The separation of these compounds was achieved by careful fractional recrystallization. The isolated mesoions **5** and **6** are stable, deeply coloured crystalline solids. The substitution positions of these products were easily determined by ¹H NMR analysis (*vide infra*). Similar reaction of the mesoionic indenide **7**⁴ with ditriflate **4** exclusively gave the benzo-annulated compound **8** in 42% yield. Spectroscopic data revealed that this compound is a 1,3-disubstituted indenide; the corresponding 1,2-disubstituted compound was not formed, probably owing to the instability of the *o*-quinonoid intermediate. Reaction of the indenide **7** with the dicationic ether salt **9**³ derived from 3-phenylsydnone gave the mixed tripolar mesoion **10** as purple crystals.

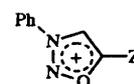
¹H NMR spectra

The ¹H NMR data of the tripolar mesoions **5**, **6**, **8** and **10** are summarized in Table 1. The cyclopentadienide ring protons of

Table 1 ¹H NMR data of tripolar mesoions **5**, **6**, **8** and **10** (*J*-values are given in Hz)

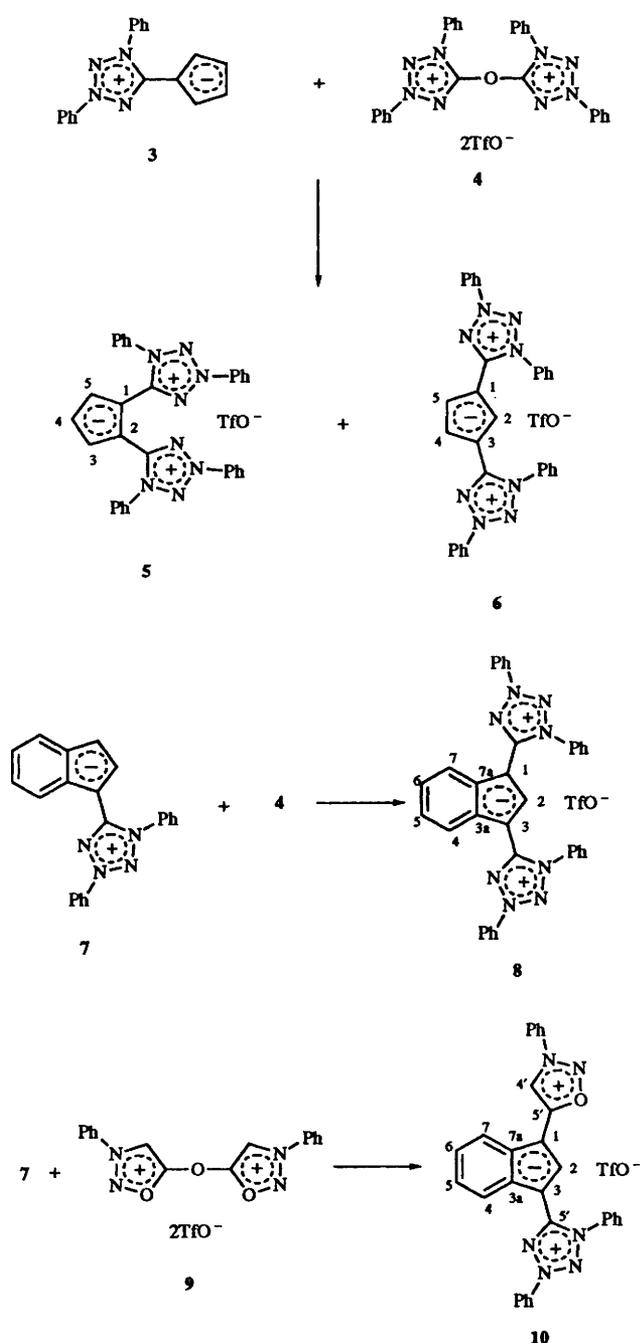
Compound	Solvent	δ_{H}
5	CDCl ₃	6.06 (1 H, t, <i>J</i> 3.8, H ⁴)
		6.26 (2 H, d, <i>J</i> 3.8, H ³ and H ⁵)
		7.68 (8 H, m, Ph)
6	CDCl ₃	8.24 (2 H, m, Ph)
		6.22 (2 H, d, <i>J</i> 2.0, H ⁴ and H ⁵)
		6.62 (1 H, t, <i>J</i> 2.0, H ²)
8	(CD ₃) ₂ SO	7.73 (8 H, m, Ph)
		8.26 (2 H, m, Ph)
		6.16 (1 H, s, H ²)
		7.31 (2 H, m, ArH)
		7.66 (8 H, m, Ph)
10	(CD ₃) ₂ SO	7.86 (8 H, m, Ph)
		8.38 (6 H, m, Ph and ArH)
		6.87 (1 H, s, H ²)
		7.32 (2 H, m, ArH)
		8.00 (13 H, m, Ph)
		8.40 (4 H, m, Ph and ArH)
		9.47 (1 H, s, oxadiazolium H)

compound **5** appear at δ 6.06 (1 H, t) and 6.26 (2 H, d) with a coupling constant *J* 3.8 Hz, whereas the isomer **6** shows signals at δ 6.22 (2 H, d) and 6.62 (1 H, t) with a smaller coupling constant, *J* 2.0 Hz, indicating that the former is a 1,2-disubstituted cyclopentadienide and the latter is a 1,3-disubstituted one. These chemical shifts are between the values of the olefinic protons of cyclopentadiene (δ 6.30 and 6.45)⁵ and cyclopentadienide anion (5.54),⁶ except for the H² proton of compound **6** which is shifted to lower field owing to the influence of the two adjacent tetrazolium rings. These data indicate the significant contribution of cyclopentadienide anion character to the ground state of the central rings of compounds **5** and **6**. The H² protons of the indenide derivatives **8** and **10** resonate at δ 6.16 and 6.87, respectively. The chemical shifts of the corresponding protons of indene and indenide anion are δ 6.50⁷ and 6.60,⁸ respectively. The oxadiazolium ring proton of compound **10** appears at much lower field (δ 9.47) compared with those of 3-phenylsydnone **11** (δ 6.78)⁹ and the dicyanomethylide derivative **12** (δ 7.69),³ indicating the lower electron density of the oxadiazolium ring of compound **10**.



11 Z = O⁻

12 = C⁻(CN)₂



Scheme 1

¹³C NMR spectra

Table 2 lists the ¹³C NMR data of the tripolar mesoionic compounds 5, 6, 8 and 10. The chemical shifts of the cyclopentadienide ring carbons of compounds 5 and 6 lie in the ranges δ_C 98.5–123.3 and 104.1–118.4, respectively. These values are shifted to higher magnetic field compared with those of the sp² carbons of cyclopentadiene (δ_C 132.2 and 132.8)¹⁰ and are almost coincident with that of cyclopentadienide anion (δ_C 102.1)¹¹ These facts indicate the considerable contribution of the tripolar (tetrazolium–cyclopentadienide–tetrazolium) canonical structure to the resonance hybrid of structures 5 and 6, as was shown by the ¹H NMR analysis. A similar tendency is also observed for the indenide compounds 8 and 10. The chemical shifts of C¹–C²–C³ carbons of compounds 8 and 10 are δ_C 95.8–

124.4–95.8 and 99.8–125.3–101.4, respectively. These values show the contribution of indenide anion (δ_C 93.4–118.1–93.4)¹² character to the ground states of the mesoions 8 and 10, though the chemical shifts of C² are shifted to lower field by 6–7 ppm compared with that of the parent anion. The chemical shifts of the olefinic carbons of indene are δ_C 133.4 and 135.2.¹³ The tetrazolium ring carbons of the tripolar compounds 5, 6, 8, and 10 resonate at δ_C 156.0–158.0, essentially the same positions of the corresponding carbon of the dipolar compounds 3 and 7 (δ_C 158.3 and 155.3).⁴ The chemical shift (δ_C 112.6) of the oxadiazolium ring carbon (C⁴) in compound 10 is more deshielded than those of 3-phenylsydnone 11 (δ_C 94.9) and its dicyanomethylide derivative 12 (δ_C 109.8), which is consistent with the results of the ¹H NMR analysis.

Experimental

Mps were determined with a hot-stage apparatus and are uncorrected. IR spectra were taken for KBr discs with a JASCO A-102 instrument. Electronic spectra were measured on a Hitachi 124 spectrophotometer. ¹H and ¹³C NMR spectra were run with a Hitachi R-24A (60 MHz) and a Varian XL-200 (50 MHz) spectrometers, respectively. Elemental analyses were performed at the Elemental Analysis Centre of Kyoto University.

1,2- and 1,3-Bis(1,3-diphenyltetrazol-5-ylidene)cyclopentadienide triflates 5 and 6

A solution of (1,3-diphenyltetrazol-5-ylidene)cyclopentadienide 3² (143 mg, 0.5 mmol) in dichloromethane (2 cm³) was added to a suspension of 5,5'-oxybis(1,3-diphenyltetrazolium) ditriflate 4³ (379 mg, 0.5 mmol) in dichloromethane (2 cm³) at 0 °C, and the mixture was stirred at 0 °C for 1 h. The reaction was quenched by the addition of water and the products were extracted with dichloromethane. The extracts were dried (Na₂SO₄) and the solvent was evaporated off under reduced pressure. The residue was chromatographed on silica gel (dichloromethane–acetone gradient 10:0–0:10) to give a mixture of title products 5 and 6 (173 mg, 53%). The ratio of compounds 5 and 6 was 3:2 by ¹H NMR analysis. Separation of products 5 and 6 was achieved by repeated fractional recrystallization from an ethanol–diethyl ether mixture.

Compound 5: red crystals; mp 177 °C (Found: C, 58.7; H, 3.8. C₃₂H₂₃F₃N₈O₃S requires C, 58.53; H, 3.53%); $\nu_{\max}/\text{cm}^{-1}$ 1574, 1528, 1354, 1266, 1150 and 1034; $\lambda_{\max}(\text{MeCN})/\text{nm}$ (log ϵ) 268 (4.46) and 357 (4.09).

Compound 6: yellow powder; mp 145 °C (Found: C, 57.1; H, 3.6; N, 16.4. C₃₂H₂₃F₃N₈O₃S·H₂O requires C, 56.97; H, 3.73; N, 16.61%); $\nu_{\max}/\text{cm}^{-1}$ 1520, 1426, 1332, 1272, 1150 and 1030; $\lambda_{\max}(\text{MeCN})/\text{nm}$ (log ϵ) 269 (4.56) and 350 (4.65).

1,3-Bis(1,3-diphenyltetrazol-5-ylidene)indenide triflate 8

This compound was prepared in 42% yield in a manner similar to compounds 5 and 6; red crystals, mp 293 °C (decomp.) (from EtOH) (Found: C, 61.2; H, 3.35; N, 15.9. C₃₆H₂₅F₃N₈O₃S requires C, 61.19; H, 3.57; N, 15.86%); $\nu_{\max}/\text{cm}^{-1}$ 1514, 1494, 1274, 1172, 1032 and 764; $\lambda_{\max}(\text{MeCN})/\text{nm}$ (log ϵ) 255 (4.69), 280 (4.51), 320 (4.07) and 391 (4.66).

1-(1,3-Diphenyltetrazol-5-ylidene)-3-(3-phenyl-1,2,3-oxadiazol-5-ylidene) indenide triflate 10

This compound was prepared in 42% yield in a manner similar to compounds 5 and 6 by the use of 5,5'-oxybis(3-phenyl-1,2,3-oxadiazolium) ditriflate 9³ as the dicationic ether salt; title product was obtained as purple crystals, mp 271 °C (decomp.) (from MeOH) (Found: C, 58.8; H, 3.3; N, 13.1. C₃₁H₂₁F₃N₆O₄S requires C, 59.05; H, 3.36; N, 13.33%); $\nu_{\max}/\text{cm}^{-1}$ 1616, 1536, 1474, 1282, 1258, 1248 and 1030;

Table 2 ^{13}C NMR data of the tripolar mesoions **5**, **6**, **8** and **10** (non-systematic numbering for the indene part of compound **10**)

Compound Solvent	5 CDCl_3	6 CDCl_3	8 ^a $(\text{CD}_3)_2\text{SO}$	10 ^a $(\text{CD}_3)_2\text{SO}$
C ¹	98.5	104.1	95.8	101.4 ^b
C ²	98.5	118.4	124.4	125.3
C ³	123.3	104.1	95.8	99.8 ^b
C ⁴	117.2	116.0	121.5	122.3 ^c
C ⁵	123.3	116.0	119.8	118.9 ^d
C ⁶			119.8	120.5 ^d
C ⁷			121.5	122.5 ^e
Phenyl <i>o</i>	121.1, 125.3	121.0, 126.1	120.9, 125.9	121.1, 122.8, 126.9
<i>m</i>	130.3, 130.5	130.5, 130.8	130.5, 130.5	130.3, 130.7, 130.9
<i>p</i>	132.2, 133.3	132.9, 133.4	132.5, 132.8	133.0, 133.4, 133.5
<i>i</i>	133.7, 135.0	133.6, 135.0	133.0, 134.9	132.9, 133.1, 135.0
Tetrazolium C ⁵	157.5	158.0	156.0	156.2
Oxadiazolium C ⁴				112.6
C ⁵				167.9

^a C^{3a} and C^{7a} peaks were not observed. ^{b-d} The individual-letter-pair values may be interchanged.

λ_{max} (MeCN)/nm (log ϵ) 253 (4.54), 282 (4.44), 312sh (4.10), 373 (4.43) and 526 (4.32).

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