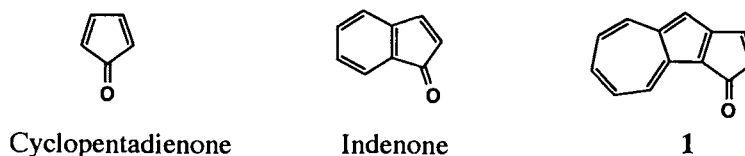


The Synthesis and Properties of Cyclopent[a]azulen-3(H)-one

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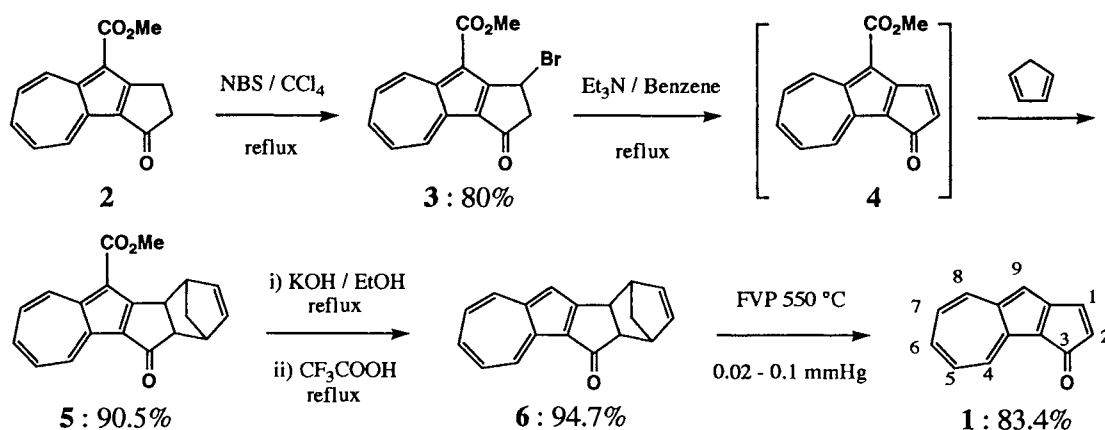
A new tricyclic π -conjugated system, cyclopent[a]-azulen-3(H)-one, was prepared by flash vacuum pyrolysis on the final step. All proton signals of this molecule were observed at higher magnetic resonance field than expected in terms of induced paramagnetic ring current in the periphery of this molecule.

Cyclopentadienone is known as an anti-aromatic compound based on the polarization of its carbonyl group.¹⁾ Although the properties of indenone have been revealed, the effect of condensation of azulene to cyclopentadienone has not been investigated.²⁾ In this paper, we wish to report the synthesis and properties of cyclopent[a]azulen-3(H)-one (**1**) which is one of azulene analogue of indenone.

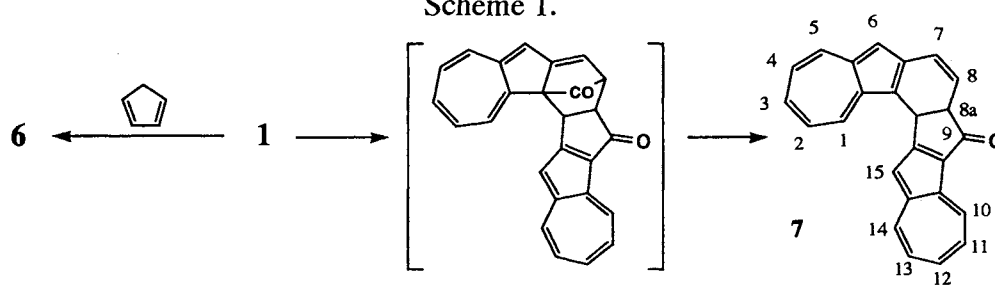


A solution of bromide **3**, which was obtained by bromination of ester **2** with N-bromosuccinimide in carbon tetrachloride, and triethylamine in benzene was refluxed for 4 h in the presence of cyclopentadiene (CPD) to give the 9-methoxycarbonyl derivative **4** of **1**.^{3,4)} This highly reactive species **4** was immediately trapped with CPD to give **5**. Hydrolysis and acid catalyzed decarboxylation afforded **6**, a formal cycloadduct of **1** to CPD. Retro-Diels-Alder reaction by heat in butyl phthalate failed because of the high reactivity of **1**. The flash vacuum pyrolysis (FVP) of **6** at 550°C under 0.02-0.10 mmHg followed by purification on a short silica gel column gave the title compound **1** as dark red crystals.^{5,6)}

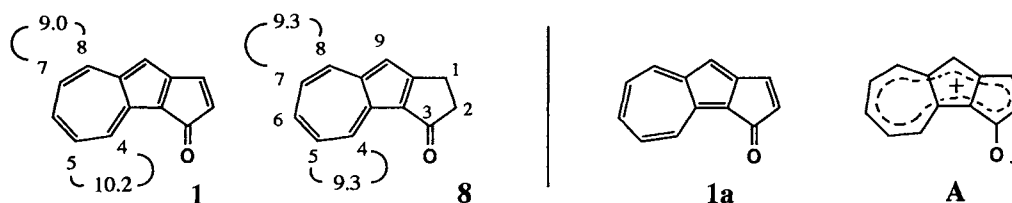
The direct synthesis of **1** from the dihydro compound **8** failed because



Scheme 1.



Scheme 2.



Coupling constants of 1 and 8, J in Hz

Scheme 3.

of the high reactivity of the azulene unit, especially at the 9-position.

The compound **1** was stable in a crystalline state, but gradually changed to **7** in solution via a dimer as shown in Scheme 2.⁷⁾ The reaction of **1** with CPD gave the cycloadduct **6**. These results were consistent with the HMO calculation shown in Fig. 1. The relatively low energy level of LUMO of **1** facilitated its dimerization and the reaction with CPD.

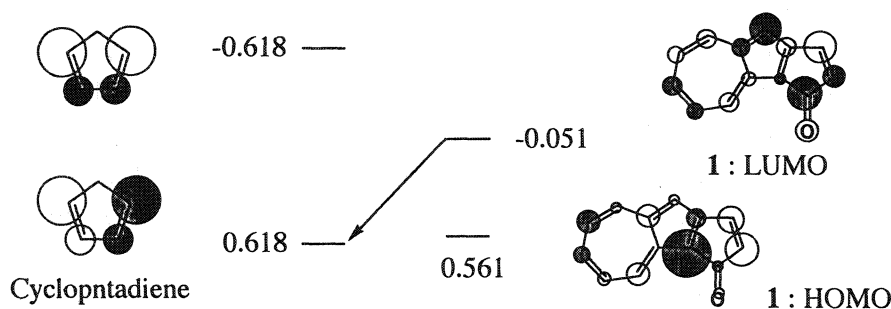
The NMR spectral data of **1** in deuteriochloroform were summarized in Table 1 and Scheme 3, together with those of the dihydro derivative **8**.³⁾ The ¹H-NMR coupling constant between H-4 and H-5 was larger than that between H-7 and H-8 as shown in Scheme 3. This fact indicated that the bond length alternation was induced on the azulene unit of **1** because of the contribution of the structure **1a** which had no unstable cyclopentadie-

none moiety.⁸⁾ All the proton magnetic resonances of the azulene unit of **1** occurred up-field by 0.31-0.68 ppm in comparison with those of the dihydro derivative **8**. On the other hand, there were no significant differences between the carbon magnetic resonances of **1** and **8**, indicating a similar distribution of electron density. So observed up-field shifts of **1** reflected the contribution of the induced peripheral 12 π -electron framework such as **A**.

Table 1. NMR Data of **1** and **8** in CDCl₃

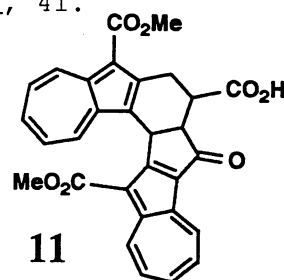
	Chemical shifts of protons of azulene unit (90 MHz, δ ppm)					
	H-4	H-5	H-6	H-7	H-8	H-9
1	8.23	7.07	7.29	7.05	7.85	6.70
8	8.91	7.38	7.69	7.43	8.32	7.04
1-8	-0.68	-0.31	-0.40	-0.38	-0.47	-0.34

	Chemical shifts of carbons of azulene unit (50 MHz, δ ppm)					
	C-4	C-5	C-6	C-7	C-8	C-9
1	133.2	129.1	137.0	130.0	136.7	113.2
8	134.8	128.0	138.1	128.7	138.0	112.1

Fig. 1. HMO Calculations of **1** and cyclopentadiene.

References

- 1) P. J. Garratt, "Aromaticity," John Wiley & Sons, New York (1986), p. 176.
- 2) P. H. Lacy and D. C. C. Smith, J. Chem. Soc., C, 1971, 41.
- 3) The ketone **2** was prepared from 9-methoxycarbonyl-1,2-trimethylene-azulene by oxidation with DDQ. Demethoxycarboxylation of **2** with phosphoric acid gave **8** T. Amemiya, M. Yasunami, and K. Takase, Chem. Lett., 1977, 587.
- 4) The treatment of **3** with lithium chloride in DMF gave **11** as a sole product.



I. Kikuchi, Master Thesis, Tohoku University, Sendai, Japan, 1979.

- 5) All new compounds gave satisfactory elemental analyses.

5: Reddish orange prisms (from MeOH); mp 193.5–195.0°C; UV (MeOH) 241 (log ϵ 4.54), 278 (4.53), 302 (sh, 4.60), 314 (4.73), 350 (sh, 3.84), 372 (sh, 3.93), 386 (4.10), and 475 nm (2.71); IR (KBr) 1690 (ester C=O) and 1666 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz, J in Hz), δ =1.80 (m, H-12), 3.42 (m, H-1), 3.46–3.58 (H-4 and 11a), 4.02 (s, OMe), 4.16 (dd, J=6.0, 4.0, H-4a), 5.48 (dd, J=6.0, 2.0, H-3), 5.96 (dd, J=6.0, 2.0, H-2), 7.66–8.03 (H-7, 8, 9), 9.06 (dd, J=9.0, 1.0, H-10), and 9.73 (dd, J=9.0, 1.0, H-6); MS m/e 304 (M^+ , 21.1%).

6: Dark red prisms (from MeOH); mp 163.5–164.0°C; UV (MeOH) 235 (sh, log ϵ 4.16), 299 (sh, 4.61), 311.5 (4.71), 355.5 (3.79), 369.5 (3.95), 389 (4.05), 507 (2.72), and 551 nm (sh, 2.58); IR (KBr) 1660 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 90 MHz, J in Hz) δ =1.76 (ddd, J=8.0, 1.5, 1.5, H-12), 1.84 (ddd, J=8.0, 1.5, 1.5, H-12), 3.32 (m, H-1, 4), 3.52 (dd, J=6.0, 4.8, H-11a), 3.95 (dd, J=6.0, 4.8, H-4a), 5.40 (dd, J=6.0, 3.0, H-2), 5.88 (dd, J=6.0, 4.8, H-3), 7.00 (s, H-5), 7.37 (ddd, J=9.5, 9.5, 1.5, H-7), 7.42 (ddd, J=9.5, 9.5, 1.5, H-9), 7.63 (dd, J=9.5, 9.5, H-8), 8.27 (d, J=9.5, H-6), and 8.82 (d, J=9.5, H-10); MS m/e 254 (M^+ , 20.6%).

1: Dark red crystals; mp 78.5–79.5°C; UV (MeOH) 223.5 (log ϵ 4.24), 252 (4.26), 304 (4.49), 313.5 (4.58), 352 (sh, 4.06), 372 (3.91), 546 (2.93), 582 (2.94), and 633 nm (2.71); IR (KBr) 1668 (C=O) cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 90 MHz, J in Hz) δ =6.03 (d, J=5.8, H-2), 6.70 (s, H-9), 7.05 (dd, J=10.2, 9.0, H-7), 7.07 (dd, J=10.2, 9.0, H-5), 7.27 (d, J=5.8, H-1), 7.29 (dd, J=10.2, 9.0, H-6), 7.85 (d, J=9.0, H-8), and 8.23 (d, J=10.2, H-4); MS m/e 180 (M^+ , 100%).

- 6) The apparatus of FVP for our purpose was arranged according to R.F.C. Brown, "Pyrolytic Method in Organic Chemistry," in "Organic Chemistry Vol. 41," Academic Press, New York (1980).

- 7) The structure of **7** was determined by $^1\text{H-NMR}$ of its deuterio derivative (**7D**). The coupling constant between H-8 and H-8a was 4.0 Hz.

- 8) Reversed coupling constant difference of these protons has been observed on benz[a]azulene which was consisted by the condensation of azulene with a stable aromatic ring.

D.J. Bertelli and P. Crews, *Tetrahedron*, **26**, 4717 (1970).

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