On the reaction of azulen-2-ylmethylene(triphenyl)phosphorane. Convenient preparation of azuleno[1,2-*f*]- and azuleno[1,2-*a*]-azulenes and their properties

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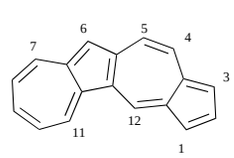
Novel azulen-2-ylmethyl(triphenyl)phosphonium bromide has been shown to be a synthon for a rapid new annulation leading to azulenoazulenes. The base treatment of the phosphonium bromide generating azulen-2-ylmethylenephosphorane 9 *in situ* and subsequent reaction with 5-(dimethylaminomethylene)cyclopenta-1,3-dienecarbaldehyde 10 and 2-chlorotropone 14 affords unsubstituted azuleno[1,2-*f*]- and azuleno[1,2-*a*]-azulenes 1 and 2, respectively. The reaction of 9 with 2-chloro-3,5,7-trideuteriotropone has also been carried out to elucidate the reaction paths leading to the formation of 2. The reaction paths involve the Michael-type addition of 9 onto 10 and 14, subsequent proton migration to regenerate the phosphorane moiety, intramolecular condensation of the formyl and carbonyl groups (Wittig reaction) and aromatization. In order to gain insight into the mechanism, PM3 calculations on compounds 9, 10 and 14 as well as on the related compound, (azulen-2-ylimino)tributylphosphorane, have been performed. The reactivity and site-selectivity of the annulation are discussed on the basis of frontier molecular orbital (FMO) theory. The electrophilic aromatic substitution of the azulenoazulenes as well as their spectroscopic and electrochemical properties have also been analyzed.

Fairly large resonance energies were predicted for the 12 isomers of cata-condensed azulenoazulenes;[1] subsequently,[1] substituted azuleno[1,2-*f*]azulene **1**[2] and azuleno[1,2-*b*]-azulene[3] were synthesized, and unsubstituted azuleno[2,1-*e*]-azulene[4] as well as azuleno[1,2-*a*]azulene **2**[5] were also prepared.



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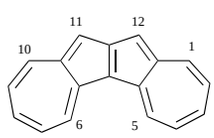

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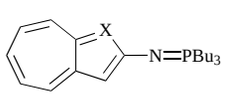
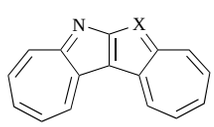


3a X = CH
3b X = N



4a X = CH
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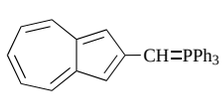


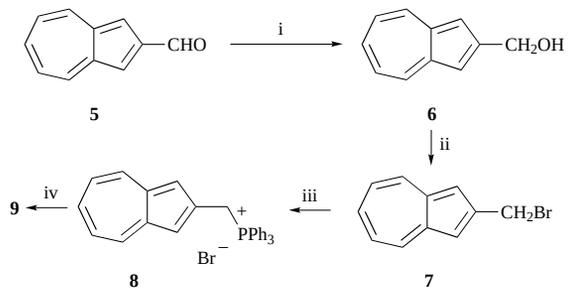
9

The singlet transitions and molecular diagrams for a derivative of **1**,[2] azuleno[1,2-*b*]azulene,[8] and **2**[8] have been calculated, and the experimental results are in good accordance with the theoretical predictions. In a series of studies of (vinylimino)-phosphoranes,[6] which provide a convenient route to pyrroles, pyridines, pyridinophanes, 1-azaazulenes, and methanocycloundeca[*b*]pyrroles, (azulen-2-ylimino)- and (1-azaazulen-2-ylimino)phosphoranes **3a** and **3b** have been found to react with 2-halogenotropones in an enamine alkylation process followed by an aza-Wittig reaction to give 6-aza- and 6,7-diaza-azuleno[1,2-*a*]azulenes **4a** and **4b**, respectively.[7] The singlet transitions and molecular diagrams for **4a** and **4b** have also been calculated, and the experimental results support the theoretical predictions.[9] In relation to the chemistry of (vinylimino)-phosphoranes, we have previously reported a novel reaction of prop-2-enylidene(triphenyl)phosphoranes with 2-substituted tropones to give azulene derivatives.[10] In this context, we planned to take advantage of the methodology for convenient preparation of azulenoazulene ring systems by utilizing the reaction of novel azulen-2-ylmethylene(triphenyl)phosphorane **9**, which is a hydrocarbon analogue of **3a** and **3b**. We describe herein the reaction of **9** with 5-(dimethylaminomethylene)-cyclopenta-1,3-dienecarbaldehyde **10** and 2-chlorotropone **14** to give azuleno[1,2-*f*]- and azuleno[1,2-*a*]-azulenes **1** and **2** in good to modest yields. In order to clarify the pathways for the formation of **2**, the reaction of 2-chloro-3,5,7-trideuteriotropone **14-D** was also studied. In order to gain insight into the mechanistic aspects, PM3 calculations on compounds **9**, **10** and **14** as well as on the related compound **3a** were also performed, and reactivity and site selectivity for **9** and **3a** are discussed on the basis of frontier molecular orbital (FMO) theory. Furthermore, electrophilic aromatic substitution of **1** and **2** as well as spectroscopic and electrochemical properties have also been studied.

Results and discussion

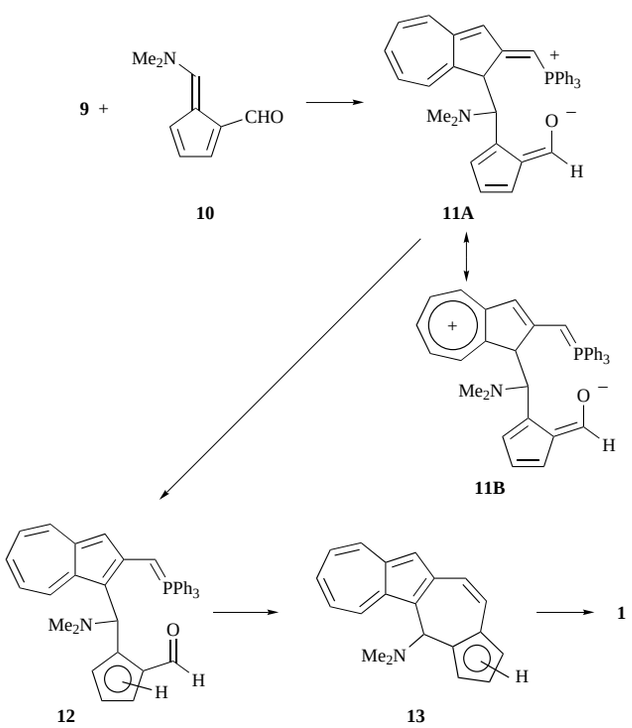
The preparation of 2-formylazulene **5** was performed through the so-called enamine method[11] utilizing cyclohepta[*b*]furan-2-one and the pyrrolidine enamine derived from 2-oxopropanal dimethyl acetal.[12] The reduction of **5** easily gave 2-hydroxymethylazulene **6**, the physical data of which are in good accordance with those reported in the literature.[13] 2-Bromomethylazulene **7**, which was prepared by the reaction of **6** with tetrabromomethane and triphenylphosphine in dry CH_2Cl_2, reacted slowly with PPh_3 to give the desired azulen-2-ylmethyl(triphenyl)phosphonium bromide **8** (Scheme 1). Although compound **7** gave no satisfactory analytical data because of its lability above 40 °C in solution, correct HRMS data were obtained for **7**. Thus the structures of **7** and **8** were determined on the basis of their physical data.

The azulen-2-ylmethylene(triphenyl)phosphorane **9**, which



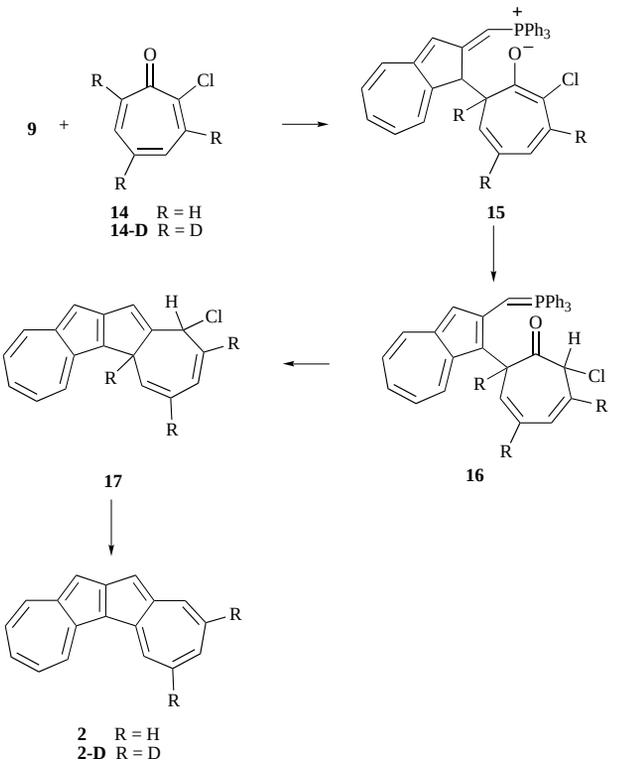
Scheme 1 *Reagents and conditions*: i, $NaBH_4$, EtOH, 0 °C, 1 h; ii, CBr_4, PPh_3, CH_2Cl_2, room temp., 0.5 h; iii, PPh_3, PhH, room temp., 6 days; iv, $KN(SiMe_3)_2$

was prepared *in situ* through the reaction of **8** with $KN(SiMe_3)_2$, reacted with **10** to give **1** in good yield. The structure of **1** was assigned on the basis of the physical data (*vide infra*). The reaction pathways are postulated as depicted in Scheme 2 in



Scheme 2

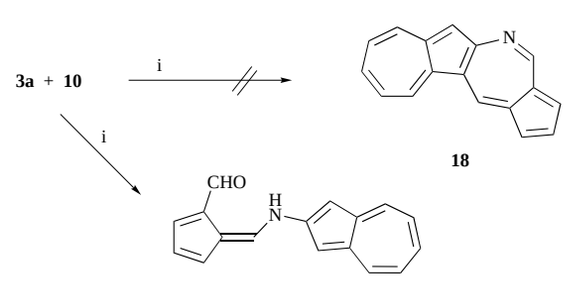
analogy with the reaction of (vinylimino)phosphorane with the aldehyde **10**.[14] A Michael-type addition of **9** onto **10** gives the intermediate **11**. The facile Michael-type addition is ascribed to the low resonance energy of azulene [12.8 kcal mol^{-1}; resonance energy per electron (REPE): 1.28 kcal mol^{-1}] as compared to, for example, that of benzene (26.1 kcal mol^{-1}; REPE: 4.35 kcal mol^{-1}),[15] as well as to a stability of the intermediate **11**, which exist as a resonance hybrid of **11A** and **11B**. The hydrogen migration in **11** regenerates the phosphorane **12**, which undergoes intramolecular Wittig reaction followed by aromatization to eliminate Me_2NH and give **1**. In a similar fashion, a solution of **9** in DMSO reacted with **14** to give **2**, which was identical with an authentic specimen obtained previously through an alternative procedure.[5] Furthermore, the reaction of **9** with **14-D**[16] afforded 2,4-dideuterioazuleno[1,2-*a*]azulene **2-D**, the structure of which was assigned on the basis of HRMS and comparison of the physical data with those of **2**.[5] The unequivocally assigned ^1H NMR spectrum clearly shows that the deuterium is located at C-2 and C-4 in **2-D**. The reaction pathways for the formation of **2** and **2-D** are also deduced to be similar to those of the reaction of (vinylimino)phosphoranes with **14** (Scheme 3).[17] The Michael-type alkylation of **9** onto



Scheme 3

C-7 of **14** and **14-D** gives the intermediate **15**. The hydrogen migration in **15** regenerates a phosphorane moiety in **16**, which undergoes intramolecular Wittig reaction to give **17**. Compound **17** undergoes aromatization eliminating HCl or DCl to give **2** and **2-D**.

As previously reported, (azulen-2-ylimino)phosphorane **3a** also reacted with **14** as in the case of **9** to give 6-azaazuleno[1,2-*a*]-azulene **4a**.[7] In contrast to the behaviour of **9** and several (vinylimino)phosphoranes,[14] however, **3a** failed to react with **10** in a Michael-type addition leading to 5-azaazuleno[1,2-*f*]azulene **18** and, instead, 6-(azulen-2-ylaminomethylene)cyclopenta-1,3-dienecarbaldehyde **19** was obtained (Scheme 4).[7] Compound **19**



Scheme 4 *Reagents and conditions*: i, toluene, reflux and adventitious water or SiO_2

probably arises from an aza-Wittig reaction of the imine nitrogen of **3a** with the formyl group of **10** or from a Michael-type addition of the imine nitrogen of **3a** onto the methylene group of **10**.[14] On consideration of calculated data by the MNDO method for a model compound (PH_3 derivative instead of PBu_3 in **3a**),[14] the site-selectivity observed for **3a** is ascribed to the high electron density on the nitrogen atom of the compound. Thus, in order to gain insight into the reactivity of compound **9** towards **10** and **14**, as compared to that of **3a**, PM3 calculations, which are also applicable for hypervalent compounds, were performed.[18] The calculated energy levels of LUMO for **10** (−0.88 eV) and **14** (−1.15 eV), and of HOMO for **9** (−6.64 eV)

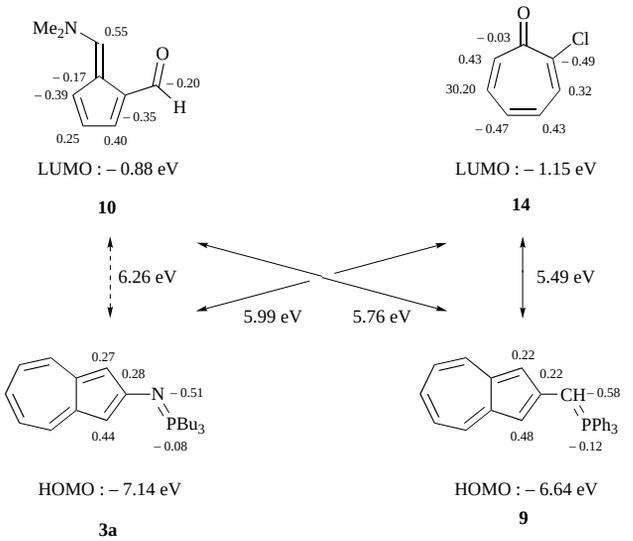


Fig. 1 Calculated energy levels and coefficients of LUMO and HOMO

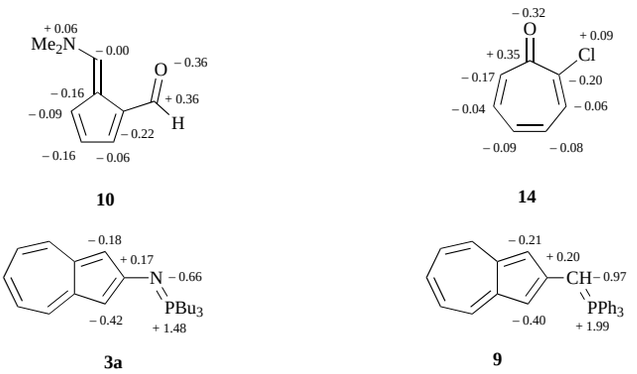
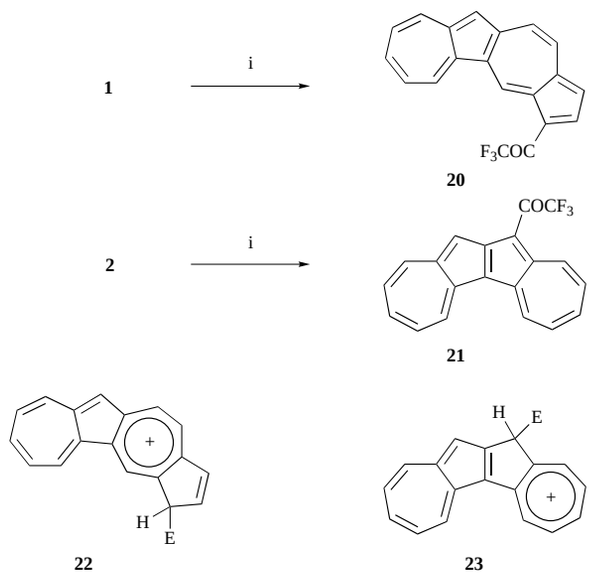


Fig. 2 Charge densities of **10**, **14**, **3a** and **9**

and **3a** (−7.14 eV) as well as coefficients of LUMO and HOMO are depicted in Fig. 1. The calculated electron densities are also summarized in Fig. 2. The energy difference (5.76 eV) of the HOMO(**9**)–LUMO(**10**) interaction is smaller than that (6.26 eV) of the HOMO(**3a**)–LUMO(**10**) interaction. The carbon adjacent to the phosphorane of **9** has the largest coefficient (0.58) in its HOMO, but its attack onto C-6 of **10** experiences considerable steric hindrance at the reaction sites and the process would not afford **1**. Thus, one may consider that C-1 having a large coefficient (0.48) of the HOMO in **9** attacks at C-6 having a large coefficient (0.55) of LUMO in **10** leading to **1** (Fig. 1 and Scheme 2). The large energy difference (6.26 eV) of HOMO(**3a**)–LUMO(**10**) presumably prevents the attack of C-1 of **3a** onto C-6 of **10** leading to **18**. Thus, high charge density (−0.66) causes attack of the nitrogen atom of **3a** onto the formyl group in **10** leading to **19** (Fig. 2 and Scheme 4).[14] The charge-controlled reaction is not observed in the reaction of **9** with **10** despite the high charge density (−0.97) of the methylene carbon atom of **9** (*cf*. Scheme 4). According to previous studies, the tropone **14** generally reacts with (vinylimino)phosphoranes as well as **3a** to give 1-azaazulenes.[6,17] Considering the present reaction of **9** with **14**, which has a low-lying LUMO as compared with that of **10**, **9** reacts with **14** readily to give **2**. The energy difference (5.49 eV) of the HOMO(**9**)–LUMO(**14**) interaction is even smaller than that (5.99 eV) of the HOMO(**3a**)–LUMO(**14**). The site-selectivity observed in the reaction of **9** with **14-D** is interesting. The LUMO coefficient of C-7 is slightly smaller than that of C-2 in **14** (and then **14-D**), but **9** attacks C-7 preferentially to give **2** (and then **2-D**) (Scheme 3). Thus, one may consider that the steric effect of the Cl substituent at C-2 prevents a preferential attack at C-2 in **14** (and then **14-D**). As reported previously, the β-carbon atom of (vinylimino)phosphorane attacks C-7 of **14**,[16] and the site-selectivity is similar to that of the nucleophilic reaction of **14**.[19] This feature is not always essential, however, and substituted (prop-2-enylidene)phosphoranes undergo reaction at both C-2 and C-7 of **14**.[10] Thus, subtle electronic and/or steric effects seem to be operative in the site-selectivity of the reaction towards **14**.

Azulene undergoes electrophilic substitution at the α-position in the smaller ring with a wide range of reagents under exceptionally mild conditions (no Lewis acid required).[20] The results are fully consistent with theoretical predictions and with the known polarization of azulenes, which concentrates electron density in the five-membered ring. Treatment of azulenoazulene **1** with $(CF_3CO)_2O$ and NEt_3 in CH_2Cl_2 at 0 °C gave **20** in good yield after recrystallization from EtOH. In a similar fashion, the reaction of **2** with $(CF_3CO)_2O$ gave **21**,[5] which was previously prepared by an alternative procedure (Scheme 5).



Scheme 5 *Reagents and conditions*: i, $(CF_3CO)_2$, 0 °C, CH_2Cl_2, 1 h

The electrophilic attack occurred at C-1 for **1** and C-11 for **2**. The result obtained for **1** is consistent with the Vilsmeier reaction of 5-cyanoazuleno[1,2-*f*]azulenes,[2] which underwent electrophilic substitution at the C-1 position, and thus the site-selectivity is discussed on the basis of ^{13}C NMR and calculated charge density as well as HOMO coefficients (*vide infra*). The high reactivity and site-selectivity of aromatic substitution in azulenes is commonly explained by the exceptional stability of an intermediate which contains a tropylium ion. The intermediacy of cycloheptazulenium ion **22**[21] (E = $COCF_3$) and tropylium ion **23** (E = $COCF_3$) in aromatic substitution onto **1** and **2** would explain the corresponding high reactivity and site-selectivity reported here for **1** and **2**. Direct support for this explanation was obtained from the ^1H NMR spectra of solutions of **1** and **2** in CF_3CO_2H. These spectra clearly indicated that quantitative protonation had occurred at C-1 of **1** and C-11 of **2** to produce **22** (E = H) and **23** (E = H), respectively (Experimental section). Quenching of the acid solutions regenerated **1** and **2**. Azulene can also be protonated to give a tropylium ion in CF_3CO_2H.[22]

The structures of **1** and **20** were characterized on the basis of their ^1H NMR, ^{13}C NMR, IR and electronic spectral data, as well as HRMS and elemental analyses. The ^1H NMR and ^{13}C NMR spectra of **1** were assigned by aid of a COSY spectrum. The average chemical shift of protons of H-7, H-8, H-9, H-10 and H-11 for **1** (δ_{av} = 7.81) is slightly lower than that of seven-membered ring protons of azulenes (δ_{av} = 7.47).[23] The observed coupling constants between neighbouring protons ($J_{8,9}$ 9.8, $J_{10,11}$ 8.8 and $J_{7,8} = J_{9,10}$ 10.3) are different. In addition, the large coupling constant $J_{4,5}$ 10.4 suggests substantial double-bond

character between C-4 and C-5. Thus, the existence of bond-length alternation in **1** is suggested. Thus, the canonical structure **1A** seems to be more important than the canonical structures **1B** and **1C**, and the contribution of peripheral 18π-conjugation in **1** seems to be small (Fig. 3). Furthermore,

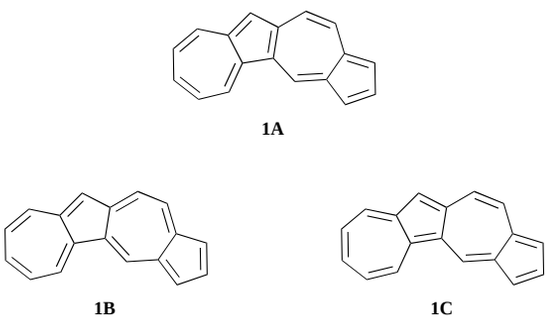


Fig. 3 Canonical structures of **1**

assignments for the ^{13}C NMR spectrum of **1** clearly indicate that the chemical shift of C-1 appearing at δ 117.9 is higher than the shifts of C-3 (δ 121.8) and C-6 (δ 122.0); this suggests a high electron density at C-1. The positions of protonation onto **1** and **2** giving **22** (E = H) and **23** (E = H) are in good agreement with the highest chemical shift of C-1 for **1** as well as of C-11 for **2**;[5] the trifluoroacetylation, therefore, also occurred at C-1 of **1** and C-11 of **2** to give **20** and **21**, respectively. Considering the calculated charge densities for **1**, C-1 (−0.17) has a slightly smaller value than C-6 (−0.18) and the same as C-3 (−0.17) (Fig. 4); however, the HOMO coefficient at C-1 (−0.37) is larger

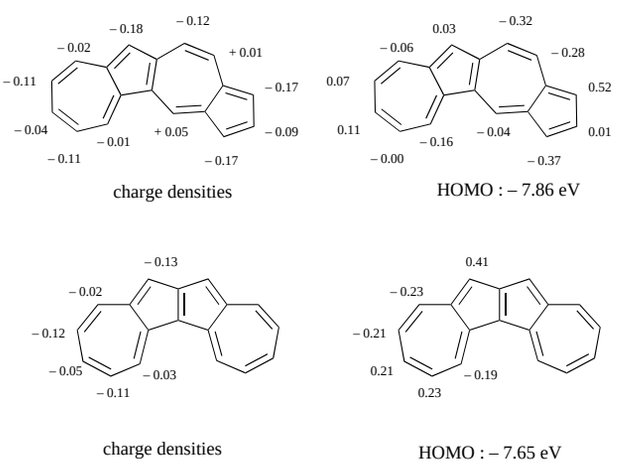


Fig. 4 Calculated charge densities and energy levels and coefficients HOMO of **1** and **2**

than that of C-6 (0.03) but smaller than that of C-3 (0.52). Thus, the calculated charge densities and HOMO coefficients seem to provide a discrepancy in the protonation and trifluoroacetylation, the site-selectivities of which are in good accordance with the chemical shifts in the ^{13}C NMR spectrum for **1**. The electrophilic substitution occurring at C-11 in **2** is in good accordance with the calculated high charge density and the large HOMO coefficient at C-11 in **2** (Fig. 4).

Although all the proton signals of **20** are shifted downfield as compared to those of **1**, the very low chemical shift of H-12 (δ_H 11.04), suggests that the $COCF_3$ group is introduced at the C-1 position, and not at the C-3 or C-6 positions. The ^{13}C NMR clearly indicates that the carbon signals of **20** are also shifted to lower field. The observed coupling constants between neighbouring protons ($J_{7,8}$ 10.2, $J_{8,9}$ 9.9, $J_{9,10}$ 9.4 and $J_{10,11}$ 8.7) are different from those of **1**, and suggest a slight decrease of bond-length alternation. The feature is not observed in compounds **2** and **21**.[5] The electronic spectrum of **1** observed is shifted to longer wavelength as compared to that of **2**.[5] The longest

Table 1 Oxidation and reduction potentials (V) and calculated energy levels of HOMO and LUMO (eV) of compounds **1**, **2**, **20** and **21**

Compd.	E^{Ox}	E^{Red}	HOMO[a]	LUMO[a]
1	0.48	−1.44	−7.86	−1.52
20	0.68	−1.16	−8.33	−2.00
2	0.53	−1.55	−7.65	−1.41
21	0.56	−1.02	−7.99	−1.81

[a] PM3 calculations were carried out by using MOPAC program.[18]

absorption maximum of **1** shifted to longer wavelength by *ca.* 10 nm compared with that of 5-cyanoazuleno[1,2-*f*]azulenes.[2] The introduction of the $COCF_3$ group causes a drastic blue shift in the electronic spectrum, and this feature is general for azulene systems. As an indication of the electronic properties of the azulenoazulene ring systems, it should be noted that the carbonyl stretching band in the IR spectra of **20** and **21** appears at 1653 and 1708 cm^{-1}, values which are lower than that for trifluoroacetylbenzene (1720 cm^{-1}), though not as low as that for trifluoroacetylazulene (1645 cm^{-1}).[19d] Thus, the CF_3CO group is suggested to be co-planar with the aromatic ring in **20**, but not co-planar in **21**.

Cyclic voltammetry of the azuleno[1,2-*f*]azulenes **1** and **20** as well as the azuleno[1,2-*a*]azulenes **2** and **21** in CH_3CN gave irreversible oxidation and reduction waves, and each of the half-height potentials were measured independently. The results and the calculated energies of HOMO and LUMO, predicted by PM3 calculations[18] are listed in Table 1. For compounds **1** and **20**, the E^{Ox} of the former exhibits a small positive value as compared with that of the latter, while the E^{Red} of the former exhibits a larger negative value than that of the latter. These features are clearly reflected in a lowering of the calculated energy levels of HOMO and LUMO of **20**, which has an electron-withdrawing $COCF_3$ group, as compared with those of **1**. These features are similar to those of the azuleno[1,2-*a*]-azulenes **2** and **21**.

In summary, the use of azulen-2-ylmethylene(triphenyl)-phosphorane **9** with 6-(dimethylaminomethylene)cyclopenta-1,3-dienecarbaldehyde **10** and 2-chlorotropone **14** is advantageous for the preparation of azulenoazulene ring systems. The reactivity of **9** was suggested on the basis of the FMO theory. Further studies concerning reaction of azulenoazulene ring systems are now underway.

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. Electronic spectra were measured on a Shimadzu UV-3101PC spectrometer. Mass spectra and high resolution mass spectra were run on JMS-AUTOMASS and JEOL JMS-SX102A spectrometers. Unless otherwise specified, ^1H NMR (90 MHz and 400 MHz) spectra were recorded on Hitachi R-90 and JNM-GSX-400 spectrometers and ^{13}C NMR (100.6 MHz) spectra were recorded on a JNM-GSX-400 spectrometer in $CDCl_3$ and the chemical shifts are given relative to internal $SiMe_4$ standard. *J* Values are given in Hz. Microanalyses were performed at the Material Characterization Central Laboratory, Waseda University. Mps were recorded on Yamato MP-21 apparatus and are uncorrected. All the reactions were performed under anhydrous conditions and dry nitrogen atmosphere.

2-Hydroxymethylazulene 6

To a stirred solution of $NaBH_4$ (29 mg, 0.75 mmol) in EtOH (3 cm^3) was added a solution of **5** (117 mg, 0.75 mmol) in EtOH (3 cm^3) at 0 °C. The mixture was further stirred for 1 h at 0 °C after which it was extracted with Et_2O. The extract was dried ($MgSO_4$) and evaporated to give **6** (119 mg, 100%) as purple plates, mp 117–118 °C (lit.,[13] mp 117–118 °C); δ_H(90 MHz) 1.87 (1H, br s), 5.11 (2H, br s), 7.16 (2H, dd, *J* 9.2, 9.5), 7.34 (2H, s), 7.56 (1H, t, *J* 9.5) and 8.25 (2H, d, *J* 9.2).

2-Bromomethylazulene 7
To a stirred solution of **6** (120 mg, 0.75 mmol) and PPh_3 (295 mg, 1.1 mmol) in dry CH_2Cl_2 (10 cm^3) was added CBr_4 (278 mg, 0.84 mmol) at RT, and the mixture was stirred for 30 min. The reaction mixture was then chromatographed on Florisil using CH_2Cl_2 as eluent to give **7** (167 mg, 100%) as violet plates, mp 114–115 °C (from PhH–hexane); δ_H(90 MHz) 4.80 (2H, s), 6.90–7.60 (5H, m) and 8.18 (2H, d, *J* 10.0); *m/z* (rel. int.) 220 (M^+, 97), 222 (M^+, 99) and 139 (100%) (Found: M^+, 219.9858. $C_{11}H_9Br$ requires *M*, 219.9888).

Azulen-2-ylmethyl(triphenyl)phosphonium bromide 8
To a stirred solution of **7** (167 mg, 0.75 mmol) in benzene (10 cm^3) was added PPh_3 (399 mg, 1.5 mmol) and the mixture was stirred for 6 days at RT. The precipitate was collected and recrystallized from CH_2Cl_2 to give the phosphonium salt **8** (340 mg, 94%) as blue plates, mp 257–258 °C (decomp.) (from CH_2Cl_2); δ_H(90 MHz) 5.56 (2H, d, *J* 15.4), 7.02 (2H, s), 7.31–7.80 (18H, m) and 8.10 (2H, d *J* 9.5) [Found: C, 72.1; H, 5.2%; $M^+ - HBr$, 402.1508. $C_{29}H_{24}PBr$ requires C, 72.06; H, 5.00%; *M*, 483.3924].

Azuleno[1,2-*f*]azulene 1
To a stirred solution of the phosphonium salt **8** (96 mg, 0.2 mmol) in DMSO (1 cm^3) was added $KN(SiMe_3)_2$ (0.5 M toluene solution; 0.4 cm^3, 0.2 mmol) and HMPA (0.2 cm^3); the violet solution turned dark red immediately. To this solution was added a solution of **10** (45 mg, 0.3 mmol) in DMSO (2 cm^3), and the mixture was stirred at 80 °C for 12 h. After this the reaction mixture was extracted with AcOEt–hexane (1:5). The extract was washed with water, dried (Na_2SO_4) and evaporated to afford a residue which was purified by TLC on silica gel (hexane–AcOEt, 5:1) to give **1** (34 mg, 75%) as dark green plates, mp 157–159 °C (decomp.) (from hexane); δ_H(400 MHz) 7.24 (1H, dd, *J* 10.3, 9.8, H-8), 7.40 (1H, dd, *J* 10.3, 8.8, H-10), 7.50 (1H, d, *J* 10.4, H-5), 7.51 (1H, dd, *J* 9.8, 10.3, H-9), 7.52 (1H, d, *J* 3.8, H-1), 7.53 (1H, s, H-6), 7.53 (1H, d, *J* 3.6, H-3), 7.60 (1H, dd, *J* 3.6, 3.8, H-2), 8.16 (1H, d, *J* 10.4, H-4), 8.17 (1H, d, *J* 10.3, H-7), 8.71 (1H, d, *J* 8.8, H-11) and 9.23 (1H, s, H-12); δ_C(100.6 MHz) 117.9 (C-1), 121.8 (C-3), 122.0 (C-6), 123.6 (C-5), 124.3 (quat. C), 126.9 (C-8), 126.9 (C-10), 129.2 (C-11), 130.5 (C-2), 131.1 (C-12), 134.0 (C-4), 134.1 (quat. C), 134.9 (C-7), 135.3 (quat. C), 135.4 (C-9), 142.5 (quat. C), 144.1 (quat. C) and 149.7 (quat. C); $\nu_{max}(CHCl_3)/cm^{-1}$ 1595 (C=O); λ_{max}(hexane)/nm (log ε) 456 (4.18), 551 (4.04), 726 (3.59), 776 (3.11) and 811 (3.15); *m/z* (rel. int.) 228 (M^+, 100) (Found: M^+, 228.0912; C, 94.5; H, 5.1%. $C_{18}H_{12}$ requires *M*, 228.0939; C, 94.70; H, 5.30%).

Azuleno[1,2-*a*]azulene 2 and 2,4-dideuterioazuleno[1,2-*a*]-azulene 2-D
To a stirred solution of the phosphonium salt (96 mg, 0.2 mmol) in DMSO (1 cm^3) was added $KN(SiMe_3)_2$ (0.5 M solution in toluene; 0.4 cm^3, 0.2 mmol). The violet solution turned dark red immediately. To this solution was added 2-chlorotropone or 2-chloro-3,5,7-trideuteriotropone (42 mg or 43 mg, 0.3 mmol) in DMSO (1 cm^3) and the mixture was stirred at 80 °C for 4 h. After this it was extracted with hexane–AcOEt (5:1). The extract was dried (Na_2SO_4) and evaporated, and the residue was purified by TLC on silica gel (hexane–AcOEt, 5:1) to give **2** (16 mg, 35%), which was identical with an authentic specimen, of **2-D** (16 mg, 35%). For **2-D**: dark brown needles, mp 152–153 °C (from EtOH); δ_H(400 MHz) 7.30 (1H, dd, *J* 8.4, 10.4, H-9), 7.39 (2H, s, H-11, 12), 7.46 (1H, dd, *J* 10.4, 8.6, H-7), 7.49 (1H, dd, *J* 8.4, 10.4, H-8), 7.49 (1H, br s, H-3), 8.31 (1H, d, *J* 10.4, H-10), 8.31 (1H, br s, H-1), 8.90 (1H, br s, H-5) and 8.91 (1H, d, *J* 8.6, H-6); *m/z* (rel. int.) 230 (M^+, 100%) (Found: M^+, 230.1097. $C_{18}H_{10}D_2$ requires *M*, 230.1065).

Trifluoroacetylation of azuleno[1,2-*f*]azulene 1
To a stirred solution of **1** (46 mg, 0.2 mmol) and NEt_3 (200 mg 2.0 mmol) was added a solution of $(CF_3CO)_2O$ (210 mg, 1.0 mmol) in CH_2Cl_2 (1 cm^3) at 0 °C. The mixture was further stirred at 0 °C for 1 h after which it was extracted with CH_2Cl_2. The extract was dried (Na_2SO_4) and evaporated to afford a residue. This was chromatographed on silica gel (hexane–AcOEt, 5:1) to give **20** (65 mg, 99%) as dark brown prisms, mp 194–196 °C (decomp.) (from EtOH); δ_H(400 MHz) 7.34 (1H, d, *J* 4.7, H-3), 7.53 (1H, dd, *J* 10.2, 9.9, H-8), 7.70 (1H, dd, *J* 9.9, 9.4, H-9), 7.76 (1H, s, H-6), 7.83 (1H, dd, *J* 9.4, 8.7, H-10), 8.04 (1H, d, *J* 10.4, H-5), 8.22–8.24 (1H, dm, *J* 4.7, H-2), 8.35 (1H, d, *J* 10.4, H-4), 8.43 (1H, d, *J* 10.2, H-7), 9.24 (1H, d, *J* 8.7, H-11) and 11.04 (1H, s, H-12); δ_C(100.6 MHz) 116.4 (CF_3), 118.8 (quat. C), 122.0, 122.7, 125.0, 128.7, 129.0, 129.4 (quat. C), 133.1, 134.1, 134.6 (quat. C), 134.9, 136.7, 138.1 (2C), 138.2 (quat. C), 143.1 (quat. C), 144.3 (quat. C), 144.4 (quat. C) and 150.3 (quat. C); $\nu_{max}(CHCl_3)/cm^{-1}$ 1653 (C=O); λ_{max}(hexane)/nm (log ε) 284 (3.33), 325 (3.14), 336 (3.14), 377 (2.98), 395 (3.04), 449 (3.44), 667 (1.75), 759 (1.17) and 7.80 (1.02); *m/z* (rel. int.) 324 (M^+, 31), 255 (100%) (Found: M^+, 324.0757; C, 73.8; H, 3.3%. $C_{20}H_{11}OF_3$ requires *M*, 324.0762; C, 74.07; H, 3.42%).

Trifluoroacetylation of azuleno[1,2-*a*]azulene 2
To a stirred solution of **2** (46 mg, 0.2 mmol) and NEt_3 (200 mg, 2.0 mmol) in CH_2Cl_2 (3 cm^3) was added a solution of $(CF_3CO)_2O$ (210 mg, 1.0 mmol) in CH_2Cl_2 (1 cm^3) at 0 °C. The mixture was further stirred at 0 °C for 1 h, after which it was extracted with CH_2Cl_2. The extract was dried (Na_2SO_4) and evaporated and the residue was purified by column chromatography on silica gel (hexane–AcOEt, 5:1) to give **21** (53 mg, 81%), which was identical with an authentic specimen.[5] For **21**: $\nu_{max}(CHCl_3)/cm^{-1}$ 1708 (C=O).

^{1}H NMR spectra of compounds 1 and 2 in trifluoroacetic acid
To the solution of **1** and **2** in $CDCl_3$ (0.6 cm^3) were added a few drops of CF_3CO_2H and the spectra were recorded on a spectrometer at ambient temperature. For **22** (E = H): a purple solution; δ_H(400 MHz) 4.37 (2H, br s), 7.54–7.57 (1H, m), 7.75–7.77 (1H, m), 8.18 (1H, t, *J* 10.0, 9.8), 8.22 (1H, s), 8.28 (1H, dd, *J* 10.5, 9.0), 8.46 (1H, dd, *J* 9.3, 10.4), 8.52 (1H, d, *J* 10.9), 8.99 (1H, d, *J* 10.4), 9.05 (1H, d, *J* 10.6), 9.74 (1H, d, *J* 9.3) and 9.90 (1H, s). For **23** (E = H): a purple solution; δ_H(400 MHz) 4.37 (2H, br s), 7.43 (1H, s), 7.88–8.04 (4H, m), 8.15–8.26 (3H, m), 8.67 (1H, d, *J* 10.4), 8.87 (1H, d, *J* 10.9) and 9.11 (1H, d, *J* 9.4).

Cyclic voltammetry of compounds 1, 2, 20 and 21
The oxidation and reduction potentials of compounds **1**, **2**, **20** and **21** were determined by means of a CV-27 voltammetry controller (BAS Co.). A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference Ag/$AgNO_3$ electrode. Nitrogen was bubbled through an acetonitrile solution (4 cm^3) of each of the compounds (1 mmol dm^{-3}) and Bu_4NClO_4 (0.1 mol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1}, and the voltammograms were recorded on a WX-1000-UM-010 (Graphtec Co.) X-Y recorder. Immediately after measurements, ferrocene (0.1 mmol) ($E_{\frac{1}{2}} = +0.083$) was added as an internal standard, and the observed cathodic or anodic peak potential was corrected with reference to this standard. The compounds exhibited no reversible reduction or oxidation waves, and each of the potentials was measured in an independent scan; the results are summarized in Table 1.

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