1 H, H-7), 12.7 (br s, 1 H, NH, exchangeable).

Anal. Calcd for $C_9H_{12}N_4O_3S$: C, 42.18; H, 4.72; N, 21.86; S, 12.51. Found: C, 42.09; H, 4.74; N, 21.81; S, 12.60.

8-(2,3-Dihydroxy-1-propyl)-4-oxo-3,4-dihydropyrazolo[1,5-*a*]-1,3,5-triazine (23). Raney nickel (1.4 g) was added to a solution of compound **21** (0.21 g, 1 mmol) in 3% NH_4OH solution (10 mL). The suspension was heated at reflux for 1.5 h. The catalyst was separated by filtration of the hot suspension and washed with hot water (4 mL). The filtrate and the washings were combined, evaporated to 2 mL, and then acidified with 10% AcOH. The precipitated product was collected by filtration, dried, and recrystallized from MeOH to afford 0.15 g (71%) of analytically pure 4-oxopyrazolotriazine **23**: mp 225–227 °C; $[\alpha]_D$ −35.6° (c 1, Me_2SO); UV λ_{max}(pH 1) 265 nm (ϵ 8900), λ_{max}(pH 8) 265 nm (ϵ 9900), λ_{max}(pH 12) 271 nm (ϵ 9780); ^1H NMR (Me_2SO-d_6) δ 2.3–2.95 (m, 2 H, H-1′), 3.31 (d, J = 5.49 Hz, 2 H, H-3′), 3.5–3.85 (m, 1 H, H-2′), 4.2–5.2 (br m, 2 H, OH-2′ and -3′, exchangeable), 7.95 (s, 1 H, H-2), 7.97 (s, 1 H, H-7).

Anal. Calcd for $C_8H_{10}N_4O_3$: C, 45.71; H, 4.80; N, 26.66. Found: C, 45.63; H, 4.83; N, 26.57.

Acknowledgment. This research was supported by United States Public Health Service Grant HD 22155 from the National Institute of Child Health and Human Development. We are grateful to Professor Ronald T. Borchard of Department of Pharmaceutical Chemistry, University of Kansas School of Pharmacy, for the determination of K_I value of compound **11** in S-adenosylhomocysteine hydrolase system. We thank Mr. Walter Schmidt for decoupling experiments which allowed us to assign the ^1H NMR spectra.

Studies in the Cycloproparene Series: On the Polarity of Alkylidenecycloproparenes

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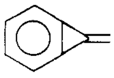
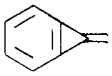
Permanent dipole moments of the alkylidenecycloproparenes **4–6**, **8–10**, and **14** fall in the range 0.4–2.6 D. The data confirm polarity in these compounds to an extent that is dependent upon the nature of the substituents attached to the exocyclic double bond. The experimentally determined values compare well with those computed for suitable model compounds at the 3-21G level. Fulvalene **14** with a cycloheptatrienylidene substituent is notable; the dipole of 1.2 D is in the *same* direction as the cyclopentadienylidene analogue **10** (2.6 D) and has the cycloproparenyl moiety as the positively charged component.

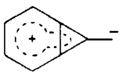
Strained organic molecules have attracted organic chemists for more than a century because of their unusual properties.[1] The strained ortho-bridged aromatics[2] and the cross-conjugated systems represented by the fulvenes[3] and radialenes[4] are interesting classes of compound in this context. The recently reported and surprisingly stable alkylidenecycloproparenes, e.g. **1**,[5] combine the structural features of these groups into a single molecule. Thus the ortho-fused **1a** may be regarded simultaneously as a benzannulated methylenecyclopropene (**1b**), a benzannulated triafulvene (**1b** ↔ **1c**), and an unusual radialene (**1d**).[6] A similar consideration of the cyclopentadienylidene homologue **2** shows that the "electron-sink" should stabilize charge separation further, cf. **2b**, when compared with **1c**. By comparison the electron-donating ability of the cycloheptatrienylidene moiety, coupled with the known stability of the cycloproparenyl anion,[5,7] could neutralize or even reverse the polarity in fulvalene **3** to favor **3b**. Thus the cycloproparenylidene substructure in these molecules is of particular interest as an ambiphile capable of stabilizing both positive and negative charge.



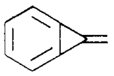
1a



1b

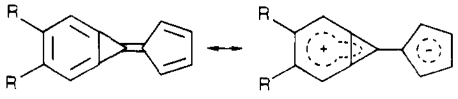


1c

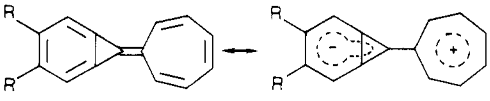


1d

We now provide details of the synthesis of the new alkylidenecycloproparenes **5**, **7**, and **9**, the hitherto unknown[8] calicene derivatives **10** and **11**, and to the best of our knowledge the first examples of triaheptafulvalenes, namely compounds **12–15**. Dipole moment measurements[9,10] have been carried out on **4–6**, **8–10**, and **14** as representative examples of compounds currently available and the results compare well with ab initio molecular orbital calculations performed at the 3-21G level for suitable model systems.



2a **2b**



3a **3b**

[†] Victoria University of Wellington.

[‡] The University of Utah.

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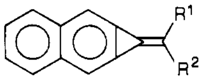
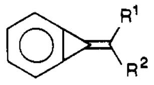
Results and Discussion

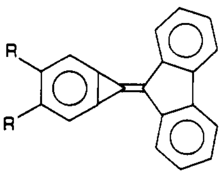
The methylenecycloproparenes **5**, **7**, and **9** were synthesized from the relevant parent cycloproparene via silylation and Peterson olefination[11] with the appropriate carbonyl-containing compound. The procedures employed were essentially those previously described[5] and they afforded these products in acceptable yields. By using 9-fluorenone in the silyl-Wittig reaction the novel calicenes[3] **10** and **11** were obtained as colored crystalline solids in yields of 38% and 92%, respectively. In analogy with this, the use of benzo[4.5]tropone gives rise to the cycloheptatrienylidene derivatives **12** (6%) and **13** (51%) while dibenzosuberenone affords homologues **14** (10%) and **15** (87%). The markedly lower isolated yields of the cyclopropabenzene derivatives, e.g., **12**, from these experiments is consistent with our earlier work and is due in part to decomposition during chromatographic separation. In no case have we been able to improve the outcome by variations in the procedures. Attempts to synthesize the parent heptafulvalenes, e.g., **3**, R = H, by use of cycloheptatrienone have been unsuccessful thus far. In each case reaction of the α-silyl anion leads to an almost quantitative recovery of unsubstituted cycloproparene as the sole isolable product.



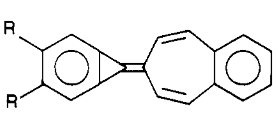
4, $R^1 = R^2 = Ph$
5, $R^1 = R^2 = p$-MeOC$_6$H$_4$
6, $R^1 = p$-MeOC$_6$H$_4$; $R^2 = H$
7, $R^1 = p$-ClC$_6$H$_4$; $R^2 = H$



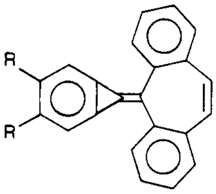
8, $R^1 = R^2 = Ph$
9, $R^1 = R^2 = p$-MeOC$_6$H$_4$



10, R=H
11, RR=benzo



12, R=H
13, RR=benzo



14, R=H
15, RR=benzo

The new alkylidenecycloproparenes reported above are colored crystalline solids which show small hypsochromic shifts in their UV absorption spectra as expected for a solvent change from nonpolar to polar.[5] Coupling of the exo- and endocyclic double bond stretching frequencies is apparent from absorption in the range 1770–1800 cm^{-1} in the IR.[6] The ^{13}C NMR spectra show the exocyclic double bond carbons in the range 105–120 ppm consistent with the fulvenes reported earlier.[3] A reasonable interpretation of these data is in support of a contribution from the charge-separated forms depicted by **1c**, **2b**, and **3b**. In order to provide unequivocal evidence for such contributions to the structures of the molecules the permanent dipole moments of compounds **4–6**, **8–10**, and **14** have been measured as representatives of the series. The very limited solubility of the naphthalene derivative **11** and the limited availability of **12** have precluded their use.

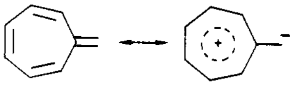
Table I. Dipole Moments of Some Alkylidenecycloproparenes[a]

	compd						
	4	**5**	**6**	**8**	**9**	**10**	**14**
μ (D)	0.41	2.4	1.4	1.0	1.9	2.6	1.2
temp (°C)	22.5	25	22	25	25	17	20

[a] Measured by the capacitance/refractive index methods, see ref 9 and 10. Values are to ±5%.

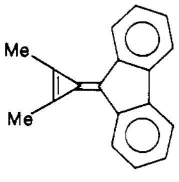
The measurement of the dipole moments followed the procedures of Guggenheim[9] and Smith[10] which require dielectric constant determination. A variable capacitance dielectric cell was built from a small trimmed capacitor such that measurements could be made with small (2 mL) volumes. The viability of the cell was established by use of suitable reference compounds (Experimental Section). Table I shows the results obtained for the cycloproparenes.

The methylenecyclopropanaphthalene **4** with unsubstituted phenyl substituents has very little polarity (μ = 0.4 D). Unfortunately, diarylmethylenecyclopropenes are not known and appropriate model compounds are lacking. It is interesting to note, however, that the polarity of this molecule is less than that of methylenecycloheptatriene (**16**) (~1.1 D),[12] which should be polarized in the same sense. By comparison the cyclopropabenzene analogue **8** is comparable to **16** and compares favorably with that calculated[13] for parent (**1**) (1.49 D) in which the cycloproparenyl moiety is the positive end of the dipole as expected.

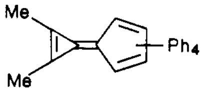


16 μ = ~ 1.1 D

The fulvalene **10**, a tribenzocalicene,[3] is a significantly polar hydrocarbon (μ = 2.6 D) because of the presence of the fluorenylidene moiety. This measured dipole is nicely consistent with that calculated[13] for benzocalicene (**2b**) (3.28 D) and is approximately one-half of the value of those of previously studied calicenes, e.g., **17** and **18**, in which the positively charged three-membered component is not fused into a benzenoid ring.[14] By comparison the cycloheptatrienylidene homologue **14** is less polar (μ = 1.2 D) but very similar to methylenecycloheptatriene (**16**). The fusion of the cycloheptatrienylidene moeity to cyclopropabenzene thus provides a compound with a small but definite and measurable, permanent dipole. It is tempting to conclude from these results that the cycloproparenyl moiety is indeed ambiphilic, stabilizing positive charge in **8** and **10**, cf. **1c**, and negative charge in **14**, cf. **3b**. However, dipole moment measurements provide the magnitude but not the direction of the effect. Molecular orbital calcu-



17 μ = 5.1 D



18 μ = 5.6 D

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(13) Apeloig, Y., personal communication. We thank Professor Apeloig (Technion, Haifa) for performing these calculations and sharing his results with us.

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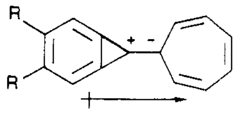
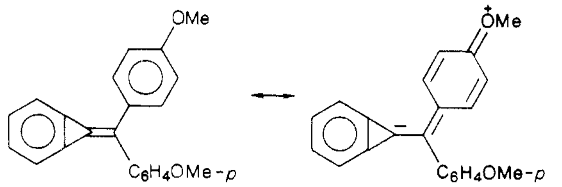
lations[13] predict **3** (R = H) to have a dipole moment of 1.12 D, *but in the direction opposite to that intuitively expected and as shown by* ***3c*** *(R = H).* It is probable that



3c $\mu = 1.12$ D

14 is similar. Moreover, the accommodation of negative charge in the seven-membered ring[15] is likely to be facilitated by a distortion of the ring from planarity.

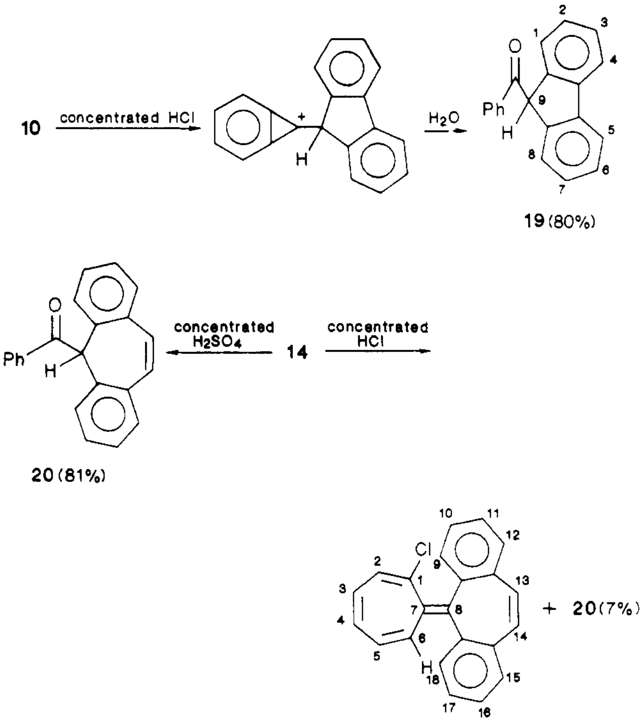
An alternative approach to an alkylidenecycloproparene with reversed polarity to **8** and **10** involves the location of suitable electron-donating functionality in the pendant phenyl rings of **8**. Thus the methoxy derivatives **5**, **6**, and **9** were prepared (vide supra).[16] As the results of Table I show, these compounds are moderately polar and it is reasonable to presume that mesomerism as in **9a** ↔ **9b** is important. The extent of mesomeric contribution from the di-*p*-anisyl derivatives **5** and **9** depends upon the twist angle θ of the anisyl substituents from the plane containing the methylenecycloproparenyl moiety.[17] As this varies with $\cos^2\theta$, each anisyl group in **5** and **9** should contribute to the net dipole less than that from an untwisted monoanisyl equivalent. The value for **5** (2.4 D) is less than double that of **6** (1.4 D) as expected on this basis.[17] In fact, if the anisyl ring in **6** is coplanar with the cycloproparenyl component, then **5** should have[18] the C8 aryl substituents twisted at an angle of ~22°. This compares with a twist angle of the phenyl substituents of **8** of ~32° in the solid state.[5]



9a **9b**

The chemistry of the benzocalicene (**10**) parallels that of **8**.[19] Thus treatment with concentrated hydrochloric acid affords 9-benzoylfluorene (**19**) in 80% yield (Chart I). The reaction is presumed to involve cleavage of the three-membered ring following protonation at the fluorenyl center.[6,19] The dibenzocycloheptatriene analogue **14** behaves similarly to give **20** only when concentrated sulfuric acid is used. The chloroheptafulvalene **21** is obtained in 76% yield from reaction with concentrated hydrochloric acid and the benozylcycloheptatriene (**20**) is formed in only 7% yield. If dilute (2 M) HCl is employed, almost equal proportions of **20** and **21** are produced. The formation of **21** can be explained by chloride ion attack at the bridge bond of cation **22** by analogy with well-established[20] cycloproparene chemistry (Scheme I), but it does not account for the different outcomes from **10** and **14** under the same conditions. This and other aspects of the chemical and physical properties of this intriguing class of hydrocarbons will form the subjects of future publications.

Chart I

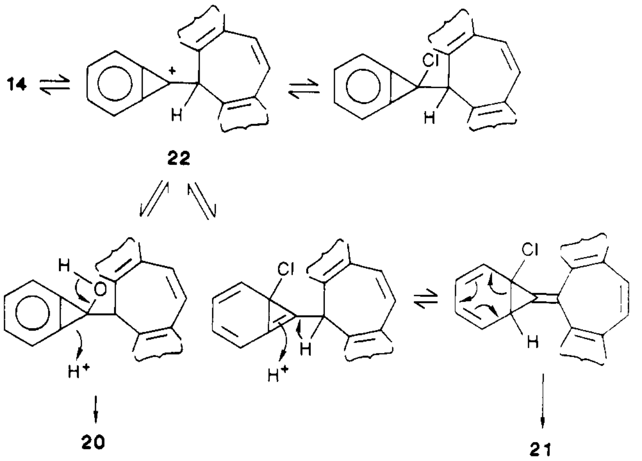


19(80%)

20(81%)

21(76%)

Scheme I



Experimental Section

For the general methods and procedures, see ref 5.

Alkylidenecycloproparenes 5, 7, and 9–15. These compounds were obtained from the appropriate 1,1-bis(trimethylsilyl)-1*H*-cycloproparene and relevant ketone by using the procedures described previously.[5]

(i) From 1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene and 4,4′-Dimethoxybenzophenone. 1-(Bis(4-methoxyphenyl)methylene)-1*H*-cyclopropa[*b*]naphthalene (5): 64%, recrystallized from dichloromethane/light petroleum ether (1:1) as orange needles; mp 134–136 °C; IR ν_{max} (KBr) 3000,

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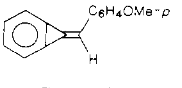
(15) Daub, J. *Chimia* **1987**, *41*, 52.

(16) The silyl-Wittig product (A) formed from cyclopropabenzene and *p*-methoxybenzaldehyde has been reported previously; see ref 5. The low stability of this compound to purification has precluded dipole moment measurements.



(17) Wepster, B. M. *Prog. Stereochem.* **1958**, *2*, 99. Dubois, J. E.; Wright, W. V. *Tetrahedron Lett.* **1967**, 3101.

(18) This results from the expression $\mu(5) = 2\mu(6)\cos^2\theta$. Thus $\cos^2\theta$ is given by 2.4/(2 × 1.4).

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2945, 2920, 2830, 1775, 1600, 1550, 1505, 1460, 1425, 1240, 1170, 1135, 1030, 830, 735 cm^{-1}; UV λ_{max} (cyclohexane) 231.5 (4.63), 243 (sh, 4.40), 256 (sh, 4.36), 280.5 (sh, 4.32), 296 (sh, 4.26), 420 (4.56), 449 nm (log ϵ 4.68); UV λ_{max} (acetonitrile) 230.5 (4.64), 254 (sh 4.38), 279.5, (4.36), 417.5 (4.57), 445 nm (log ϵ 4.66); ^{1}H NMR δ 3.83 (s, 2 × OMe), 6.9–7.9 (complex m, 14 H); ^{13}C NMR δ 55.3 (q, 2 × OMe), 106.0 (d, C2/C7), 109.5 (s, C1), 113.9 (d, C11/C13, C17/C19), 119.8 (s, C8), 126.4 (d, C4/C5) 127.8 (s, C1a/C7a), 128.5 (d, C3/C6), 129.4 (d, C10/C14, C16/C20), 132.2 (s, C9/C15), 138.6 (s, C2a/C6a), 159.1 (s, C12/C18); mass spectrum (70 eV), *m/e* (relative intensity) 364 (100, M), 349 (M – Me, 57); μ (benzene, 25 °C) 2.4 D. Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.7; H, 5.5. Found: C, 86.0; H, 5.5.

(ii) From 1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene and 4-Chlorobenzaldehyde. 1-((4-Chlorophenyl)methylene)-1*H*-cyclopropa[*b*]naphthalene (7): 48%, recrystallized from dichloromethane/light petroleum ether (1:1) as pale yellow microcrystals; mp 154–156 °C; IR ν_{max} (KBr) 1775, 1580, 1475, 1380, 1245, 1170, 1135, 1080, 850, 735 cm^{-1}; UV λ_{max} (cyclohexane) 230 (4.63), 285 (4.36), 296.5 (4.64), 424.5 nm (log ϵ 4.74); UV λ_{max} (acetonitrile) 228.5 (4.75), 284.5 (4.52), 393 (4.76), 419.5 nm (log ϵ 4.83); ^{1}H NMR δ 6.49 (s, H8), 7.2–7.9 (complex m, 10 H); ^{13}C NMR δ 105.6 (d, C8), 108.5/108.6 (d, C2/C7), 112.4 (s, C1), 125.3 (s, C1a or C7a), 126.9/127.0 (d, C4/C5), 127.4 (d, C11/C13), 128.9 (d, C3/C6, C10/C14), 132.2(5) (s, C12), 136.4 (s, C9), 138.4/139.1 (s, C2a/C6a); mass spectrum (70 eV), *m/e* (relative intensity) 264/262 (35.8/100, M), 226 (71, M – HCl). Anal. Calcd for $C_{18}H_{11}Cl$: C, 82.3; H, 4.2; Cl, 13.5. Found: C, 82.0; H, 4.2; Cl, 13.6.

(iii) From Bicyclo[4.1.0]hepta-1,3,5-triene[21] and 4,4′-Dimethoxybenzophenone. 7-(Bis(4-methoxyphenyl)methylene)-7*H*-bicyclo[4.1.0]hepta-1,3,5-triene (9): 34%, recrystallized from light petroleum ether as yellow microcrystals; mp 118–119 °C; IR ν_{max} (KBr) 3000, 2960, 2830, 1780, 1618, 1508, 1465, 1450, 1385, 1330, 1282, 1248, 1170, 1150, 1030, 830, 735 cm^{-1}; UV λ_{max} (cyclohexane) 233.5 (4.06), 265 (sh, 4.20), 273 (4.20), 392.5 (4.28), 413 nm (sh, log ϵ 4.21); UV λ_{max} (acetonitrile) 226 (4.17), 268 (4.38), 389 (4.41), 408 nm (sh, log ϵ 4.33); ^{1}H NMR δ 3.84 (s, 2 × OMe), 6.8–7.6 (complex m, 12 H); ^{13}C NMR δ 55.3 (q, 2 × OMe), 110.0 (d, C2/C5), 110.7 (s, C7 or C8), 111.2 (s, C8 or C7), 113.9 (d, C11/C13, C17/C19), 128.8 (d, C10/C14, C16/C20), 132.6 (d, C3/C4), 132.8 (s, C1/C6, C9/C15), 158.4 (s, C12/C18); mass spectrum (70 eV), *m/e* relative intensity) 314 (100, M), 299 (75, M – Me); μ (benzene, 25 °C) 1.9 D. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.0; H, 5.7. Found: C, 84.0; H, 5.6.

(iv) From Bicyclo[4.1.0]hepta-1,3,5-triene and 9-Fluorenone. 7-(5*H*-Dibenzo[*a*,*d*]cyclopentan-5-ylidene)-7*H*-bicyclo[4.1.0]hepta-1,3,5-triene (10): 38%, recrystallized from pentane as yellow needles; mp 180–181 °C (sealed capillary, under N_2); IR ν_{max} (KBr) 3040, 1795, 1776, 1540, 1440, 1405, 1354, 1327, 1212, 1143, 1031, 1005, 999, 976, 930, 858, 765, 734, 720 cm^{-1}; UV λ_{max} (cyclohexane) 239 (4.69), 248 (4.58), 264.5 (4.35), 275.5 (4.44), 392 (4.40), 411 (4.57), 438 nm (log ϵ 4.63); UV λ_{max} (acetonitrile) 238.5 (4.68), 246.5 (4.61), 261.5 (4.24), 273 (4.16), 388 (4.40), 407.5 (4.56), 432 nm (log ϵ 4.51); ^{1}H NMR δ 7.1–7.6 (complex m, 10 H), 7.7–8.0 (complex m, 4 H); ^{13}C NMR δ 107.9 (s, C7 or C8), 110.7 (s, C8 or C7), 112.6 (d, C2/C5), 120.0, 120.6, 125.9, 126.4, 135.3 (all 2 × aromatic CH), 131.8 (s, C1/C6), 137.9(5) (s, C12a/C12b), 138.8 (5) (s, C8a/C16a); mass spectrum (70 eV), *m/e* (relative intensity) 253/252 (22/100, M), 251 (13), 250 (40); μ (benzene, 17 °C) 2.6 D. Anal. Calcd for $C_{20}H_{12}$: C, 95.2; H, 4.8. Found: C, 95.4; H, 4.9 (5).

(v) From 1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene and 9-Fluorenone. 1-(5*H*-Dibenzo[*a*,*d*]cyclopentan-5-ylidene)-1*H*-cyclopropa[*b*]naphthalene (11): 92%, recrystallized from dichloromethane/light petroleum ether (1:2) as orange needles; mp 259–260 °C; IR ν_{max} (KBr) 3055, 1780, 1442, 1416, 1332, 1248, 1172, 1128, 944, 936, 860, 843, 768, 743, 722, 616 cm^{-1}; UV λ_{max} (cyclohexane) 278.5 (4.65) 290.5 (4.28), 435.5 (4.79), 470.5 nm (log ϵ 5.00); UV λ_{max} (acetonitrile) 278.5 (4.55), 287 (4.30), 433.5 (4.73), 466.5 nm (log ϵ 4.87); ^{1}H NMR δ 7.34–7.61 (complex m, 6 H), 7.76–8.20 (complex m, 8 H); ^{13}C NMR δ 109.6 (C2/C7), 120.2, 121.7, 126.9, 127.3, 127.5, 129.2 (all 2 × aromatic CH), 138.6, 139.1, 139.9 (all s); mass spectrum (70 eV), *m/e* (relative intensity) 303/302 (27/100, M), 301 (11), 300 (33), 299 (6), 298 (12). Anal. Calcd for $C_{24}H_{14}$: C, 95.3; H, 4.7. Found: C, 95.1; H, 4.5.

(vi) From Bicyclo[4.1.0]hepta-1,3,5-triene and 7*H*-Benzocycloheptadien-7-one. 7-(7*H*-Bicyclo[4.1.0]hepta-1,3,5-trien-7-ylidene)-7*H*-benzocyclohepta-5,8-diene (12): 6%, recrystallized from pentane as red crystals; mp 128–129 °C; IR ν_{max} (KBr) 3040, 1765, 1505, 1446, 1382, 1348, 1323, 1309, 1244, 1150, 980, 939, 875, 804, 728, 662 cm^{-1}; UV λ_{max} (cyclohexane) 235.5 (4.68), 283 (4.31), 394 (4.34), 419 (4.69), 439 (4.55), 451.5 nm (log ϵ 4.79); UV λ_{max} (acetonitrile) 252 (4.62), 281.5 (4.31), 391 (4.33), 414 (4.61), 433 (4.48), 444 nm (log ϵ 4.64); ^{1}H NMR (CD_2Cl_2) δ 5.76 and 6.16 (J_{AB} = 12.0 Hz, H5/H9, H6/H8), 6.6–7.4 (complex m, 8H); ^{13}C NMR (CCl_4) δ 109.0 (C11/C14), 127.8 (5), 129.1, 131.5, 132.0, 132.3 (all 2 × CH), 133.6 (s, C10a/C14a), 138.1 (s, C4a/C9a); mass spectrum (70 eV), *m/e* (relative intensity) 229/228 (20/100, M), 227 (34), 226 (83), 225 (11), 224 (12). Anal. Calcd for $C_{18}H_{12}\cdot SiO_2$:[22] C, 75.0; H, 4.2. Found: C, 74.9; H, 4.4.

(vii) From 1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene and 7*H*-Benzocycloheptadien-7-one. 7-(1*H*-Cyclopropa[*b*]naphthalen-1-ylidene)-7*H*-benzocyclohepta-5,8-diene (13): 51%, recrystallized from dichloromethane/pentane (2:1) as red crystals; mp 232 °C dec; IR ν_{max} (KBr) 3050, 3020, 1780, 1720, 1630, 1583, 1556, 1537, 1449, 1389, 1342, 1249, 1169, 1145, 948, 849, 813, 742 cm^{-1}; Laser-Raman IR ν_{max} 1774, 1643, 1574, 1507, 1350, 1332, 1262, 900, 756 cm^{-1}; UV λ_{max} (cyclohexane) 236 (4.44), 272 (4.46), 407 (4.09), 438 (4.58), 458 (4.35), 475 nm (log ϵ 4.92); UV λ_{max} (acetonitrile) 236 (4.50), 271 (4.54), 404 (4.17), 434 (4.63), 454 (4.45), 470 nm (log ϵ 4.93); ^{1}H NMR δ 6.04 and 6.46 (d, J_{AB} = 16.0 Hz, H5/H9, H6/H8), 6.88–6.93 (m, 2 H), 7.02–7.06 (m, 2 H) 7.28 (s, H11/H16), 7.37–7.43 (m, 2 H), 7.74–7.79 (m, 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 279–278 (26/100, M), 277 (18), 276 (43), 275 (6), 274 (11); exact mass calcd for $C_{22}H_{14}$ *m/e* 278.1095, found *m/e* 278.1077).

(viii) From Bicyclo[4.1.0]hepta-1,3,5-triene and 5*H*-Dibenzo[*a*,*d*]cyclohept-10-en-5-one. 5-(7*H*-Bicyclo[4.1.0]hepta-1,3,5-trien-7-ylidene)-5*H*-dibenzo[*a*,*d*]cyclohept-10-ene (14): 10%, recrystallized from pentane as yellow crystals; mp 158–158.5 °C; IR ν_{max} (KBr) 3040, 1773, 1484, 1450, 1427, 1344, 1318, 1227, 1146, 1104, 980, 945, 861, 799, 752, 746, 727, 660 cm^{-1}; UV λ_{max} (cyclohexane) 253 (4.663), 308 (3.82), 383 nm (log ϵ 4.31); UV λ_{max} (acetonitrile) 250 (4.60), 299 (3.89), 376 nm (log ϵ 4.30); ^{1}H NMR δ 6.69 (s, H10/H11), 7.08–7.65 (complex m, 12 H); ^{13}C NMR δ 110.7 (C13/C18), 111.7 (5) (s, C5 or C12), 117.1 (s, C12 or C5), 126.8, 127.6, 128.8, 129.7, 132.0, 133.2 (all 2 × CH), 132.9 (s, C12a/C18a), 135.6 (s, C9a/C11a), 14097 (s, C4a/C5a); mass spectrum (70 eV), *m/e* (relative intensity) 279/278 (24/100, M), 277 (68), 27 (97), 275 (12), 274 (28); μ (benzene, 20 °C) 1.2 D. Anal. Calcd for $C_{22}H_{14}$: C, 94.9; H, 5.1. Found: C, 94.9; H, 5.0.

(ix) From 1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene and 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-one. 5-(1*H*-Cyclopropa[*b*]naphthalen-1-ylidene)-5*H*-dibenzo[*a*,*d*]cyclohept-10-ene (15): 87%, recrystallized from dichloromethane/hexane (1:1) as a bright yellow crystalline solid; mp 190–191 °C; IR ν_{max} (KBr) 3030, 3005, 1776, 1582, 1478, 1410, 1338, 1242, 1168, 1130, 1092, 940, 848, 790, 750, 738 cm^{-1}; Laser-Raman IR ν_{max} 1798, 1777, 1604, 1576, 1557, 1520, 1363, 1285, 1020, 809, 755, 534, 515, 483, 419, 232, 186, 156, 116, 63 cm^{-1}; UV λ_{max} (cyclohexane) 228 (4.59), 254 (4.58), 280 (4.25), 414 nm (log ϵ 4.29); UV λ_{max} (acetonitrile) 226 (4.68), 252 (4.65), 278 (4.36), 411 nm (log ϵ 4.39); ^{1}H NMR δ 6.76 (s, H10/H11), 7.18–7.46 (complex m, 10 H), 7.66–7.88 (complex m, 4 H); ^{13}C NMR δ 107.0 (C13/C18), 115.9 (s, C5 or C12), 120.2 (s, C12 or C5), 126.5, 127.4, 127.5, 128.6, 128.7, 129.7, 131.7 (all 2 × CH), 135.2, 138.5, 139.6 (all s); mass spectrum (70 eV), *m/e* (relative intensity) 329/328 (27/100, M), 327 (75), 326 (89), 325 (11), 324 (26). Anal. Calcd for $C_{26}H_{16}$: C, 95.1; H, 4.9. Found: C, 95.2; H, 4.7.

(x) From 1,1-Bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene and Tropone. Reaction of tropone with the α-silyl carbanion generated in the usual[5] way and under a variety of

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[21] Fusion nomenclature requires cyclopropabenzene to be named systematically as bicyclo[4.1.0]hepta-1,3,5-triene.

[22] Following chromatography over silica gel, this compound crystallizes with 1 molar equiv of silica gel. Silicon peaks were recorded in the energy dispersive X-ray spectrum of the compound obtained in a Philips 508 scanning electron microscope. We thank Dr. D. Nelson, Electron Microscope Facility, Victoria University, for this experiment.

conditions led to the formation of cyclopropa[*b*]naphthalene as the sole isolable product in yields ranging from 82% to 95%; mp, mmp 86–87 °C.

Reactions of the Fulvalenes 10 and 14 with Acids. (i) 9*H*-Fluoren-9-ylphenylmethanone (19).[23] To a stirred solution of **10** (22 mg, 0.1 mmol) in acetonitrile (20 mL) was added hydrochloric acid (12 M), 0.1 mL, 1.2 mmol) at room temperature. After 6.5 h an additional aliquot of acid was added, and stirring was continued for a further 19 h. Excess acid was neutralized (solid sodium bicarbonate) and the solution concentrated to a slurry which was partitioned between dichloromethane and water (100 mL, 1:1). The separated aqueous phase was washed with dichloromethane (50 mL) and the combined organic solution washed with water (2 × 50 mL), dried ($MgSO_4$), and concentrated in vacuum. Preparative TLC of the residue (dichloromethane-/light petroleum ether, 3:2) resulted in a band, R_f 0.25, which when extracted gave 9*H*-fluoren-9-ylphenylmethanone (**19**): 19 mg, 80%, recrystallized from light petroleum ether as straw-colored needles; mp 135–136 °C (lit.[24,25] mp 138 °C); mass spectrum (70 eV), *m/e* (relative intensity) 270 (5, M), 165 (10, M – PhCO), 105 (100, PhCO), 77 (28, Ph).

(ii) (5*H*-Dibenzo[*a*,*d*]cyclohept-10-en-5-yl)phenylmethanone (20). To a stirred solution of **14** (28 mg. 0.1 mmol) in acetonitrile (20 mL) was added sulfuric acid (18 M, 0.11 mL; 2.0 mmol). After 4 h at room temperature, workup as described in (i) above gave a residue which was triturated with hexane to afford **(5*H*-dibenzo[*a*,*d*]cyclohept-10-en-5-yl)phenylmethanone (20)**: 24 mg, 81%, as colorless crystals; mp 124.5–125 °C; IR ν_{max} (KBr) 3015, 2921, 1672, 1596, 1578, 1491, 1446, 1435, 1259, 1244, 1209, 1177, 1000, 965, 876, 821, 794, 765, 745, 692, 614 cm^{-1}; ^{1}H NMR δ 5.50 (s, H5), 6.87 (s, H10/H11), 7.18–7.65 (complex m, 13 H); ^{13}C NMR δ 62.4 (C5), 126.9, 127.9, 128.3, 128.8, 129.1, 129.4, 131.0 (all 2 × CH), 131.6 (CH), 135.1, 136.8 (both s, C4a/C5a and C9a/C11a) 138.1 (2, ipso Ph), 197.1 (s, CO); mass spectrum (70 eV), *m/e* (relative intensity) 296 (6, M), 192/191 (17/100; M – PhCO), 189 16, M– PhCO – 2 H), 165 (9, M – PhCO – C_2H_{28} 105 (3, PhCO), 77 (6, Ph). Anal. Calcd for $C_{22}H_{16}O$: C, 89.1 (5); H, 5.4 (5). Found: C, 89.3; H, 5.1 (5).

(iii) 5-(1-Chlorocyclohepta-1,3,5-trien-7-ylidene)-5*H*-dibenzo[*a*,*d*]cyclohept-10-ene (21) and (5*H*-Dibenzo[*a*,*d*]-cyclohept-10-en-5-yl)phenylmethanone (20). (a) To a stirred solution of **14** (56 mg, 0.2 mmol) in acetonitrile (40 mL) was added hydrochloric acid (10 M, 0.4 mL, 4.0 mmol). The solution turned golden-yellow immediately upon the addition and was stirred at room temperature for 15 min, during which time considerable discoloration occurred. Workup as described in (i) above gave, in order of elution from radial chromatography (dichloromethylene/light petroleum ether, 2:3) the following.

5-(1-Chlorocyclohepta-1,3,5-trien-7-ylidene)-5*H*-dibenzo[*a*,*d*]cyclohept-10-ene (21): 48 mg, 76%, recrystallized from hexane as yellow crystals; mp 130.5–132 °C; IR ν_{max} (KBr) 3017, 1625, 1593, 1485, 1474, 1430, 1408, 1384, 1343, 1157, 1110, 1095, 1030, 972, 950, 924, 910, 882, 862, 854, 800, 776, 768, 740, 727, 678, 657, 605 cm^{-1}; ^{1}H NMR δ 5.64 (d, J = 11 Hz, H14), 5.98–6.62 (complex m, 4 H, H15–H18), 6.92 (s, H10/H11), 7.21–7.37 (m, 8 H); ^{13}C NMR δ 127.0, 127.3, 127.4, 127.6, 128.3, 128.8, 129.6, 131.3 (all CH), 217.7, 130.8 (both 2 × CH), 128.6 (3 × CH), 126.1, 133.6, 134.4, 134.7, 136.8, 138.7, 140.4 (all s); mass spectrum (70 eV), *m/e* (relative intensity) 316/314 (13/40, M); 280/279 (23/100, M – Cl), 278 (52), 277 (34), 276 (41). Anal. Calcd for $C_{22}H_{15}Cl$: C, 83.9; H, 4.8; Cl, 11.3. Found: C, 84.0; H, 4.6; Cl, 11.4.

(5*H*-Dibenzo[*a*,*d*]cyclohept-10-en-5-yl)phenylmethanone (20): 4 mg, 7%, as a colorless crystalline solid, mp, mmp 122–124 °C.

(b) The reaction of **14** (28 mg, 0.1 mmol) in acetonitrile (20 mL) with hydrochloric acid (2 M, 1.0 mL, 2.0 mmol) for 2.5 h at room temperature and workup as described in (i) above gave methanone **20** (11 mg, 41%), mp, mmp 124–125 °C, and cycloheptatrienylidecycloheptatriene **21** (14 mg, 44%), mp, mmp 130–131 °C.

Dipole Moment Determinations. Dipole moments were determined for benzene solutions by the method of Guggenheim[9] and Smith[10] using a small variable dielectric capacitance cell (volume ~2 mL). Impedence readings were taken with the cell open and closed employing a Hewlett Packard 913A vector impedence meter operating at either 1.0 or 0.7 MHz. The recordings were made at ambient temperature. AR grade benzene was used for all solutions (0.05–0.15 M) and the compounds studied were analtically pure samples (C, H). Refractive index measurements were made on an Abbe 60/ED refractometer. All mathematical transformations[9,10] were made on a Hewlett Packard 75C programmed microprocessor. The dipole moments of the cycloproparenes are recorded in Table I. The following compounds were used as standards and their dipole moments were recorded several times during the study. Diphenyl sulfone: μ = 5.01 D at 20 °C [lit.[24] 4.98 D], 4.98 D at 25 °C [lit.[24] 5.04 D]. 2-Hydroxynaphthalene: μ = 1.47 D at 23 °C [lit.[24] 1.30 D at 18 °C; 1.53 D at 25 °C]. Phenyl benzoate: μ = 1.79 D at 20 °C [lit.[24] 1.86 D at 22 °C].

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