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THE SYNTHESIS AND PROPERTIES OF AZULENO[1,2-*d*]BICYCLO[5.4.1]DODECA-1,4,6,8,9a-PENTAEN-3-ONE AND ITS CATIONIC SPECIES

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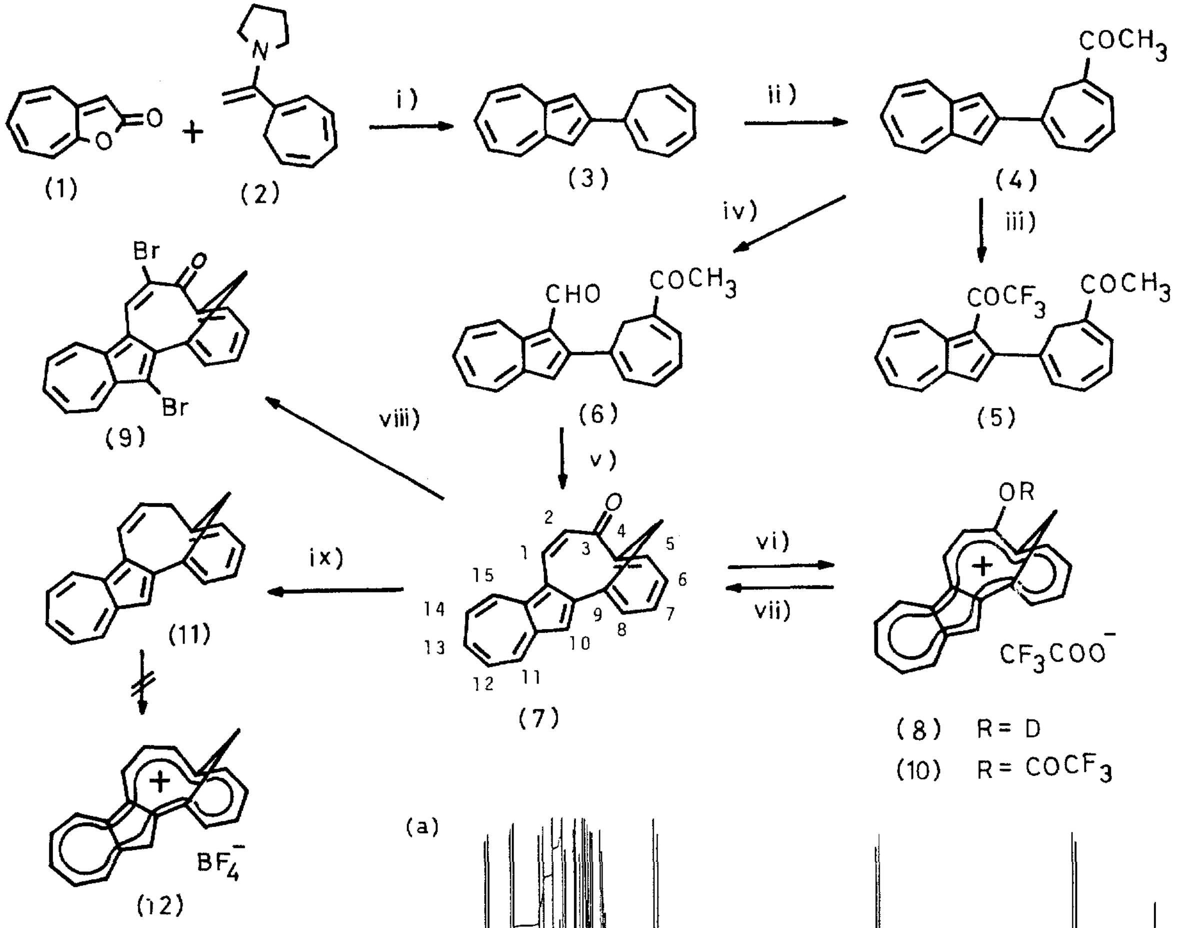
Summary: The titled azuleno-annulenone was synthesized and in strong acid its protonated cationic species was generated, which is the first 18-pi electron diatropic condensed bridged annulene as shown in its ^{1}H-NMR spectrum.

Although the syntheses and properties of the condensed 18-pi electron systems such as azulenoazulenes have been reported,1) no condensed system such as azulene fused with bridged annulenone has so far been investigated. In this paper we wish to report the synthesis and properties of titled azuleno-bridged annulenone and its cationic species generated in strong acid.

The synthetic pathway is shown in scheme 1. The reaction of 2H-cyclohepta-[*b*]furan-2-one (1) with pyrrolidino enamine of 1-acetylcyclohepta-1,3,5-triene (2) in dry toluene at reflux for 4-5 h gave 2-(cyclohepta-1,3,5-trienyl)azulene (3) [dark green needles, mp 116-117 °C] in 35 % yield.2) The acetylation of 3 by the action of acetyl chloride and zinc chloride in dichloromethane at ice cooling for 2 h furnished 2-(6-acetylcyclohepta-1,3,5-trienyl)azulene (4) exclusively [dark green needles, mp 95.5-97.5 °C] in 78 % yield. Treatment of 4 with trifluoroacetic anhydride in tetrachloromethane at r. t. for 30 min, gave a product trifluoroacetylated at 1-position of azulene moiety (5) as deep reddish needles in 9.5 % yield. The intramolecular cyclization of 5 under various aldol condensation conditions was failed. Now an alternate route was sought. The reaction of 4 with Vilsmeier reagent successfully gave (6) which was selectively formylated at 1-position of azulene moiety [deep reddish green needles, mp 78-78.5 °C] in 80 % yield. After many attempts, the intramolecular cyclization of 6 by aldol condensation (piperidine-acetic acid in benzene at reflux for 8 h) was successfully achieved to give (7) [deep green cluster needles, mp 140-141 °C] in 75 % yield.

SCHEME I



i) toluene/reflux/5 h,
ii) AcCl/$ZnCl_2$/0°C/3 h,
iii) $(CF_3CO)_2O/CCl_4$/
r. t./30 min.,
iv) $POCl_3$/DMF/r. t./3 h,
v) AcOH/piperidine/
benzene/reflux/8 h,
vi) CF_3COOD or $(CF_3CO)_2O$,
vii) excess H_2O,
viii) Br_2/NEt_3/r. t./
30 min., ix) $LiAlH_4$/
$AlCl_3$/THF/-30°C/2 h.

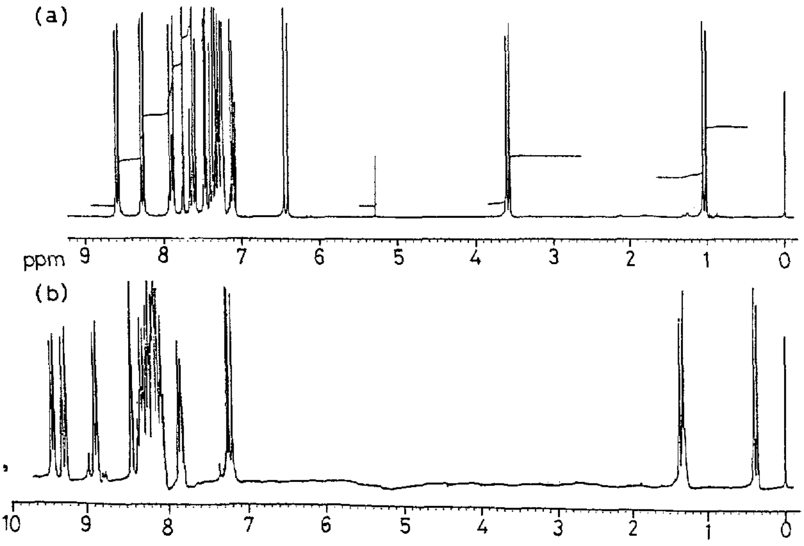


Fig. 1 The 200 MHz ^{1}H-NMR spectra of (a)(7) in $CDCl_3$ and (b)(8) in CF_3COOD.

The ^{1}H-chemical shifts of outer ring protons of 7 resonated at slightly lower field than those of 6, e. g., those of the protons on 3-, 4-, 5-, 6-, and 7-positions shifted to lower field in ca. 0.27 ppm, and those of the bridged methylene protons resonated at 3.58 and 1.03 ppm, which are at lower field than those of 4,9-methano[11]annulenone.$^{3)}$ It suggests small contribution of a dipolar structure with a peripheral 18-pi electrons as shown in Fig. 1. Whereas, all outer protons in the cationic part of cationic species 8 generated in such strong acid as trifluoroacetic acid-d appear at lower field (av. ca, 8.57 ppm) than those of 7, where those of the annulenone moiety and the azulene moiety are very close to those of the cation of 4,9-methano[11]annulenone, and the corresponding protonated cation of 3H-cyclohepta[a]azulene-3-one ,$^{4)}$ respectively. Furthermore, the ^{1}H-chemical shifts of bridged methylene protons of 8 are observed at fairly high field [1.34 and 0.38 ppm (J=12.5Hz)] as the case of [11]annulenone. Accordingly, it is evident that the cationic species 8 is peripheral 18-pi electron diatropic on the basis of the above results. Thus, the peripheral resonance stability of the cationic species 8 was revealed, and was further supported by the following reactions.

The bromination of 7 gave an unexpected dibromo compound (9) [brown needles, mp 199.5-201 °C] in 80 % yield. The formation scheme is concievable as follows. Initially, bromine added to 1,2-positions of 7 followed by the electrophilic substitution of bromine at 10-position on azulene moiety, and finally the dehydrobromination occurred at 1,2-position. The ^{1}H-chemical shifts of 9 are similar to those of 7. The ^{1}H-NMR spectrum of 7 in $(CF_3CO)_2O$ and $CDCl_3$ (1:1) was identical with that of 8, indicating the formation of the trifluoroacetylated cation (10) instead of the substitution. Treatment of the reaction mixture with excess H_2O recovered only the starting material.

The reduction of 7 with AlH_3 in dry THF furnished (11) in 68 % yield. However, an attempt to generate a parent cationic species (12) by the reaction of 11 with trityl fluoroborate was failed. An alternate synthesis of this cation is under investigation.

Spectral data of new compounds.
3: IR (KBr) 1635w, 815vs, 782s, 728vs cm^{-1}; ^{1}H-NMR (CCl_4-TMS) δ =7.80 (d, J=9.30Hz, 2H), 7.14 (s, 2H), 7.11 (m, 2H), 6.78 (m, 3H), 6.41 (m, 1H), 6.41 (m, 1H), 5.78 (m, 1H), 2.88 (d, J=6.92Hz, 2H); MS m/z 218 (M^+, 76 %), 202 (100 %); 4: IR (KBr) 3050w, 1653vs, 1272s, 1215s, 738vs cm^{-1}; ^{1}H-NMR (CCl_4-TMS) δ= 8.00 (d, J=8.72Hz, 2H), 7.46 (s, 2H), 7.01 (m, 6H), 6.55 (dd, J=9.62, 6.01Hz, 1H), 3.10 (s, 2H), 2.24 (s, 3H); MS m/z 260 (M^+, 100 %), 217 (79 %, M^+-$COCH_3$); 5: IR (KBr) 3040w, 1647vs, 1258s, 1139s, 725m cm^{-1}; ^{1}H-NMR ($CDCl_3$-TMS) δ= 8.64 (d, J=10.10Hz, 1H), 8.24 (d, J=9.62Hz, 1H), 6.86 (m, 8H), 3.27 (s, 2H), 2.61 (s, 3H); MS m/z 356 (M^+, 40 %), 287 (49 %), 215 (100 %); 6: IR (KBr) 3050w, 1643vs, 1450s, 1388s, 745s, cm^{-1}; ^{1}H-NMR ($CDCl_3$-TMS) δ = 10.04 (s, 1H), 9.62 (d, J=9.32Hz, 1H), 8.24 (d, J=9.91Hz, 1H), 7.70 (s, 1H), 7.41 (m, 4H), 6.76 (m,

3H), 3.22 (s, 2H), 2.34 (s, 3H); MS m/z 288 (M^+, 63 %), 215 (100 %); UV (CH_2Cl_2) λ_{max} 625sh (log ε=2.85), 565 (2.95), 535 (2.93), 340 (4.34), 230nm (4.25); 7: IR (KBr) 3030w, 1615s, 1559s, 1408s, 1360s, 739s, cm^{-1}; ^{1}H-NMR ($CDCl_3$-TMS) δ = 8.59 (d, J=9.76Hz, H-15), 8.26 (d, J=10.01Hz, H-11), 7.90 (d, J=14.64 Hz, H-1), 7.76 (s, H-10), 7.63 (t, J=9.77Hz, H-13), 7.48 (d, J=6.35Hz, H-5), 7.37 (t, J=9.76Hz, H-14 or H-12), 7.28 (m, H-12 or H-14, H-7, & H-8), 7.12 (ddd, J=1.22, 6.35, & 10.01Hz, H-6), 6.43 (d, J=14.64Hz, H-2), 3.58 (d, J=12.00Hz, H-H_e), 1.03 (d, J=12.00Hz, H-H_z); MS m/z 270 (M^+, 59 %), 242 (100 %); UV λ_{max}(CH_2Cl_2) 715sh(log ε=1.86), 640(2.49), 586(2.28), 550(2.51), 440(3.42), 386(4.31), 351sh(4.08), 305(3.89), 229nm(3.77); 8: ^{1}H-NMR (CF_3COOD-TMS) δ = 9.40 (d, J=9.16 Hz, H-15), 9.26 (d, J=13.19 Hz, H-1), 8.88 (d, J=10.26 Hz, H-11), 8.44 (s, H-10), 8.32 (dd, J=9.16, 9.34 Hz, H-13), 8.23 (d, J=7.33 Hz, H-5 or H-8), 8.15 (m, H-7 or H-6, H-12, & H-14), 8.06 (d, J=7.33 Hz, H-8 or H-5), 7.84 (dd, J=8.79, 7.33 Hz, H-6 or H-7), 7.22 (d, J=13.19 Hz, H-2), 1.34 (d, J=12.50 Hz, H-H_e), 0.38 (d, J=12.50 Hz, H-H_z); UV λ_{max}(CF_3COOH) 700sh(log ε=2.02), 683sh(2.57), 568(3.78), 442(4.26), 384(4.26), 352sh(4.08), 291(3.56), 258nm(3.66); 9: IR (KBr) 3030w, 1619vs, 1575s, 1521s, 1369s, 1340s, 1296s, 1137s, 835s, 742s, 732s cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ = 8.78 (s, 1H), 8.50 (d, J=7.65 Hz, 1H), 8.36 (d, J=10.23 Hz, 1H), 7.43 (m, 7H), 3.26 (d, J=13.86 Hz, 1H), 1.13 (d, J=13.86 Hz, 1H); MS m/z 430, 428, 426 (M^+, 9.9 %, 18.2 %, 10.0 %).

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