67. Structural Detail and Thermal Bond Relocation of a Sterically Strained Cyclononatetraene

Preliminary Communication

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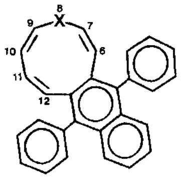
Summary

The X-ray crystallographic molecular dimensions and thermal response of the 5,13-diphenyl-cyclonona[*b*]naphthalene **1a**, are described.

A most revealing spectroscopic feature of 5,13-diphenyl-8*H*-cyclonona[*b*]-naphthalene (**1a**), an intermediate in the synthesis of ketone **1b** [1], is the magnetic nonequivalence of its methylene protons which appear in the NMR. spectrum as two well-separated ($\Delta\delta = 0.35$ ppm) 1*H*-multiplets. The obvious implication of this fact is that the C_9-moiety of **1a** lacks the conformational mobility normally associated with medium and large rings and thus that the molecule is conformationally rigid[2]).

We have examined **1a** in this connection and we now briefly record information pertaining to the molecular dimensions and shape of **1a** and its response to thermal activation.



1a $X = CH_2$
1b $X = CO$

The molecular dimensions and shape of **1a** obtained from a single crystal X-ray determination[3]) are summarized in the *Figure*. The listed information confirms the

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[2]) This sharply contrasts the relatively flexible nature of the C_9-moiety in the parent compound, 7*H*-benzocyclononene [2] whose CH_2-unit gives rise to a single, slightly broadened, 2*H* triplet in the ^1H-NMR. spectrum.

[3]) The details of the X-ray study kindly performed by Prof. *M. Haque* and his associates will be supplied in the full account of the crystallographic work.

Torsion angles in the C_9-ring

Segment	*Angle* (θ)
C–C(12)–C(11)–C(10)	+3.4°
C(12)–C(11)–C(10)–C(9)	–48.5°
C(11)–C(10)–C(9)–CH_2	0°
C(10)–C(9)–CH_2–C(7)	–31.1°
C(9)–CH_2–C(7)–C(6)	+94.2°
CH_2–C(7)–C(6)–C	–3.3°
C(7)–C(6)–C–C	–77.5°
C(6)–C–C–C(12)	–7.3°
C–C–C(12)–C(11)	+79.2°

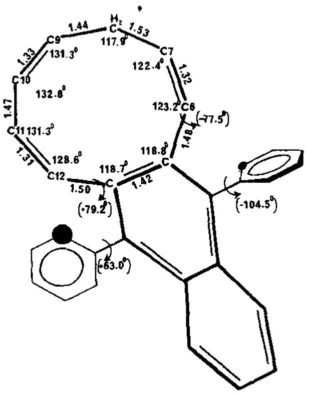

Fig. *X-Ray molecular dimensions and torsion angles for 5,13-diphenyl-8*H*-cyclonona[b]naphthalene* (**1a**)[3]

expectation of a heavily puckered frame with well-developed helicity[4]. Further, the C_9-moiety is clearly distorted as attested by the wider-than-normal bond angles of its butadiene and methylene segments and the striking difference in length between the two structurally related bonds C(8),C(9) (1.444 (6) Å) and C(8),C(7) (1.528 (6) Å). The observed distortion is undoubtedly steric in nature arising chiefly from the presence of the two phenyl appendages and particularly the one on the butadiene side of the molecule which is associated with a smaller torsion angle (63°) and thus larger effective size than its *para*-counterpart (– 104.5°).

The skeletal rigidity of **1a** enhances its thermal reactivity[5], the molecule readily and cleanly undergoing ring contraction at *ca.* 100° ($k = 4.9 \times 10^{-5}\,s^{-1}$; $\Delta G^{\neq} = 30.3$ kcal/mol at 112.4°) to produce the bright yellow 1-buta-1,3-dien-1-yl-1*H*-cyclopentanaphthalene (**2**) [m.p. 176–177°. – UV. (C_6H_{14}): 310 (14,800), 300 (14,500), 273 (20,400), 255 (31,100), 243 (40,300). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 4.68 (*t*, J(d,c) $= J$(d,e) $= 10.4$, 1 H, H–C(d)); 4.75 (*d*, $J = 10.2$, 1 H, H–C(c)); 4.89 (*d*, $J = 10.0$, 1 H, H'–C(g)); 4.97 (*d*, $J = 16.0$, 1 H, H–C(g)); 5.77 (*t*, J(e,d) $= J$(e,f) $= 10.4$, 1 H, H–C(e)); 6.29 (*d*, $J = 5.6$, 1 H, H–C(b)); ≈6.3 (*m*, 1 H, H–C(f)); 6.72 (*d*, $J = 5.6$, 1 H, H–C(a)); 7.2–7.8 (*m*, 14 H, arom. H). – ^{13}C-NMR. (90 MHz, $CDCl_3$, H-coupled): 49.12 (*d*, $J \approx 130$, C(c)); 117.00 (*t*, $J \approx 160$, C(g)); 125–142 (sp^2-centers). – MS.: 370 (100, M^+)].

In turn, when heated at *ca.* 140° compound **2** undergoes bond relocation to a mixture of geometrically isomeric naphthofulvenes **3** and **4** in proportions dependent on the length and temperature of thermal exposure, **4** being invariably favored on prolonged heating. Pure **4** was obtained as an air sensitive solid [UV. (C_6H_{14}): 400 (10,200), 326 (22,000), 305 (64,000), 235 (35,000). – ^{1}H-NMR. (360 MHz, $CDCl_3$)[6]: 1.85 (*d*, $J = 7.0$, 3 H, CH_3); 5.55 (*d*×*qa*, J(f,CH_3) $= 7.0$, J(f,e) $= 14.0$, 1 H, H–C(f)); 5.70 (*d*, $J = 10.5$, 1 H, H–C(d)); 6.55 (*d*×*d*, J(e,f)

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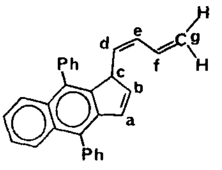
[4] Note the oppositely directed bonds linking the C_9-segment of **1a** with the naphthalene moiety, *i.e.*, C(12a),C(12) and C(5a),C(6), which are associated with large, nearly equal, torsion angles, +79.2° and – 77.5°, respectively.

[5] 7*H*-Benzocyclononene, the benzo analog of **1a**, is thermally stable under these conditions.

[6] The determination of certain coupling constants required double irradiation.

$= 14.0$, J(e,d) $= 10.5$, 1 H, H–C(e)); 6.75 (*d*, $J = 5.5$, 1 H, H–C(b)); 7.00 (*d*, $J = 5.5$, 1 H, H–C(a)); 7.3-7.8 (*m*, 14 H, arom. H). - ^{13}C-NMR. (90 MHz, $CDCl_3$, H-coupled): 18.67 (*qa*, $J = 130$, CH_3); 125-140 (sp^2-centers). - MS.: 370 (12.6, M^+)] by column chromatography (Al_2O_3, *ca.* $-15°$) of a (2:1)-mixture of **4** and **3** produced upon heating **2** in benzene at 200° for 11 h. On the other hand, because of its pronounced tendency to isomerize to **4** under a variety of conditions, **3** [^{1}H-NMR. (360 MHz, $CDCl_3$): 1.40 (*d*, $J = 7.5$, 3 H, CH_3); 5.68 (*d*×*qa*, J(f,CH_3) $= 7.5$, J(f,e) $= 10.5$, 1 H, H–C(f)); 6.18 (*d*, $J = 12.0$, 1 H, H–C(d)); 6.52 (*d*×*d*, J(e,f) $= 10.5$, J(e,d) $= 12.0$, 1 H, H–C(e)); 6.75 (*d*, $J = 5.5$, 1 H, H–C(b)); 6.95 (*d*, $J = 5.5$, 1 H, H–C(a)); 7.3-7.8 (*m*, 14 H, arom. H). - ^{13}C-NMR. (90 MHz, $CDCl_3$): 13.15 (CH_3); 125-140 (sp^2-centers)] could not be isolated pure but was obtained in suitably enriched form from a two component thermolysate containing $< 15\%$ **4** and generated by heating **1a** in benzene successively at 140° and 200° each time for 35 min.



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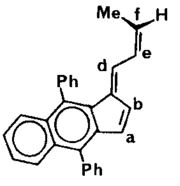

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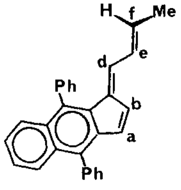

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The general structures of **3** and **4** follow from the NMR. spectra and the specific stereochemical assignments, *i.e.*, *cis*- and *trans*-methyl groups in **3** and **4**, respectively, were deduced from the fact that J(e,f) is 10.5 Hz in **3** and 14.0 Hz in **4** and that the methyl group of **3**, being shielded by the adjacent phenyl appendage, resonates at higher fields than its counterpart in **4**. Chemically, the structures of **3** and **4** and their relationship to **2** were established through catalytic hydrogenation (Pd/C, 1 Torr H_2) of a (1:1)-mixture of **3** and **4** to a single product (white solid, m.p. 123-125°) identical (GC., ^{1}H-NMR.) with a sample obtained on catalytic hydrogenation of **2** under similar conditions.

The thermal conversion of **1a** to **2** may be viewed as a rather rare 1,5-shift of a vinylic group entailing rupture of the long bond to CH_2, *i.e.* C(8),C(7), 1.53 Å rather than its shorter counterpart, C(8), C(9), 1.44 Å. The conversion of **2** to **3** very likely proceeds *via* 1,5-H-shift from C(c) to C(g) in the *cisoid*-form of **2**, *i.e.* **5**, to yield **6** the sterically congested *cisoid*-variant of **3**. In fact the steric strain (CH_3, H(b) interaction) plaguing **6** may very well be the chief factor responsible for the surprisingly facile ($\Delta G^{\neq} \approx 32$ kcal/mol at 140°) overall (*Z*)/(*E*)-isomerization of **3** to **4**[7].

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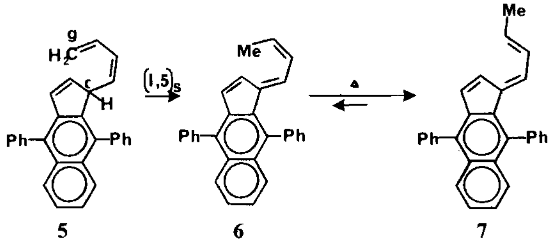
[7] The destabilization of **3** relative to **4** may be viewed as an entropy effect due to the steric demands imposed by the **3** to **6** rotational conversion which ought to be substantially greater than those of the corresponding conversion of **4** to its *cisoid*-form **7**. In fact, the greater contribution of the *cisoid*-form of **4** as compared to that of **3**, *i.e.*, **6**, is clearly indicated by the fact that J(d,e) (**4**) $= 12.0$ Hz $>$ J(d,e) (**3**) $= 10.5$ Hz.



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REFERENCES

[1] *A. G. Anastassiou, H. S. Kasmai & M. Sabahi*, J. Chem. Soc., Chem. Commun. *1979*, 1031.
[2] *A. G. Anastassiou, S. S. Libsch & R. C. Griffith*, Tetrahedron Lett. *1973*, 3103.