

Figure 1. Plot of the data in Table I according to the rate law for a unimolecular reversible reaction with $K_{eq} = 1$ ($k = (1/2t)\ln(0.5/0.5 - \beta)$).¹⁵

eq 3; however, the experimental data do not yet justify such a conclusion. Intermediates other than azulene, e.g., **2** or **3**, could equally well account for the observed scrambling of α and β carbon atoms (but not γ) in naphthalene. The highly strained prismane (**2**) can presumably be excluded on energetic grounds, for it must certainly lie more than 86 kcal/mol above naphthalene,¹⁷ but the benzvalene (**3**) appears no more strained than the isomeric bicyclobutane **1**. At present, we see no reason to favor intermediate **1** in preference to **3** except that conservation of orbital symmetry⁵ forbids concerted valence isomerization of naphthalene to the latter in the ground state.¹⁸ Suitable double-labeling experiments could distinguish between these two possibilities.



Even if naphthalene does automerize via azulene, as suggested by the agreement between $\Delta G^\ddagger_{\text{predicted}}$ and $\Delta G^\ddagger_{\text{exptl}}$, the mechanism of interconversion of those two aromatic hydrocarbons still remains open to speculation. We are currently studying the thermal isomerization of azulene-¹³C to test the mechanistic hypothesis in eq 2.

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References and Notes

- (1) Full details of this work can be found in the Ph.D. thesis (part II) of G. K. Agopian, UCLA, 1975; a preliminary account was presented at the 31st Northwest Regional Meeting of the American Chemical Society, Reno, Nev., June 14, 1976.
- (2) The term "automerization" was introduced by Balaban^{3a} to describe those isomerizations which are degenerate in the absence of a label. Ironically, the aluminum chloride catalyzed automerization of naphthalene reported in that paper^{3a} was subsequently shown to be incorrect.^{3b,c}
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- (6) The mechanistic hypothesis shown in eq 2 was apparently conceived independently also by H. J. Reich, R. B. Woodward, and R. W. Alder (personal communication from each) and M. Prislowski.^{4c}
- (7) Reported as $\Delta H^\ddagger = 48.8 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = -5.3 \pm 3.6$ eu (375–425 °C); E. Heilbronner in "Nonbenzenoid Aromatic Compounds", D. Ginsburg, Ed., Interscience, New York, N.Y., 1959, p 264.
- (8) The difference in free energy between azulene and naphthalene is almost completely independent of temperature: $\Delta\Delta G^\circ = -30.66$ kcal/mol (298 K) and -30.57 kcal/mol (1000 K); $\Delta\Delta H^\circ = -30.82$ kcal/mol (298 K) and -30.36 kcal/mol (1000 K); $\Delta\Delta S^\circ = -0.53$ eu (298 K) and $+0.01$ eu (1000 K); D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969.
- (9) Naphthalene, 90% enriched with ¹³C in one of the α positions, was synthesized by known methods.^{3c}
- (10) The pyrolysis apparatus consists of a quartz tube packed with quartz chips. A constant stream of nitrogen served to carry the naphthalene through the hot zone as it slowly sublimed at atmospheric pressure.
- (11) The values listed in Table I were determined by a known method¹² involving mass spectral analysis of naphthoquinone (experimental error $\pm 4\%$). The α : β isomer ratio was also checked in certain cases by ¹³C NMR and ¹H NMR (of the ¹³C satellites associated with the α and β proton resonance signals) and agreed well with those values listed in Table I.
- (12) V. A. Koptuyug, I. S. Isaev, and M. I. Gorfinkel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 845 (1970); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 794 (1970); *Chem. Abstr.*, **73**, 44501 (1970); J. H. Bowie, D. W. Cameron, and D. H. Williams, *J. Am. Chem. Soc.*, **87**, 5094 (1965).
- (13) The possibility that these results reflect a surface-catalyzed reaction rather than a strictly thermal, gas phase reaction cannot be rigorously excluded; however, omission of the quartz packing chips from the pyrolysis tube did not change the results significantly (i.e., 5.0-sec contact time \rightarrow 61% α , 36% β , 3% γ). The entire pyrolysis apparatus was base washed prior to use.
- (14) We have also observed the "automerization" of 1-methylnaphthalene, 2-methylnaphthalene, naphthalene-1-d, and naphthalene-2-d under similar conditions.
- (15) K. J. Laidler, "Chemical Kinetics", 2nd ed, McGraw-Hill, New York, N.Y., 1965; t is taken as the contact time and β is the fraction of β isomer.
- (16) The experimental value of 86 kcal/mol for ΔG^\ddagger should be considered an upper limit since the contact times in Table I may overestimate the interval during which the material is actually at 1035 °C.
- (17) J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968); *Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968).
- (18) See, however, M. J. S. Dewar and S. Kirshner, *J. Am. Chem. Soc.*, **97**, 2931, 2932 (1975); N. J. Turro, C. A. Renner, T. J. Katz, K. B. Wiberg, and H. A. Connon, *Tetrahedron Lett.*, 4133 (1976). Our experimental data do not exclude the intriguing possibility that this automerization involves internal conversion of "hot" naphthalene from the vibrationally excited ground state to the first singlet electronic excited state (S_1 , $E = 90.8$ kcal/mol above S_0);¹⁹ reversible isomerization to the benzvalene **3** would be symmetry allowed in the excited state;⁵ cf. L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 675 (1965).
- (19) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 295.

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Dibenzo[gh,op]nonalenide Dianion. A Novel Aromatic System Derived from Nonalene

Sir:

Fused conjugated systems containing $4n$ π electrons, similarly to the monocyclic cyclooctatetraene,¹ may acquire aromatic character either by oxidation to the corresponding dication, or by formation of the dianion. These ions behave like peripheral aromatic systems containing $(4n + 2)$ π electrons.² Only the heptalenide dianion³ and the pentalenide dianion⁴ are known in this series.⁵ Benzannulated derivatives, e.g., the dibenzo[cd,gh]pentalenide dianion, have been prepared and exhibit aromatic character.⁶ We wish to report the synthesis and properties of the dibenzo[gh,op]nonalenide dianion (**1**), the first derivative of the hitherto unknown nonalenide dianion

2 (and the corresponding nonalene), which manifests aromatic character.

A bis-Wittig reaction⁷ was carried out between biphenyl-2,2':6,6'-tetracarboxaldehyde⁸ and 1,3-bis(triphenylphosphonium)propane dibromide in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene affording 7*H*-dibenzo[*a,c*]cyclononene-1,13-dicarboxaldehyde (**3**,⁹ 12% yield); mp 30 °C; *m/e* 274 (M, 19%); $\nu_{\text{max}}^{\text{Nujol}}$ 1700 cm^{-1} (C=O stretching); ¹H NMR δ (CDCl₃)¹⁰ 2.67 (tt, 2 H, $J_1 = 6.0$, $J_2 = 1.5$ Hz, H₇, H_{7'}), 5.60 (td, 2 H, $J_1 = 12.0$, $J_2 = 7.0$ Hz, H₆, H₈), 6.16 (td, 2 H, $J_1 = 12.0$, $J_2 = 1.5$ Hz, H₅, H₉), 7.45 (m, 4 H, H₃, H₄, H₁₀, H₁₁), 7.85 (dd, 2 H, $J_1 = 6.0$, $J_2 = 2.0$ Hz, H₂, H₁₂), 9.56 ppm (s, 2 H, formyl). Under similar conditions, the consecutive Wittig reaction of **3** with the same phosphonium salt yielded 6,14-dihydrodibenzo[*gh,op*]nonalene (**4**, 7% yield)⁹; mp 112 °C, *m/e* 283 (M + 1), 282 (M, 70%), 281, 268, 254, 240 (100%); $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 224 (ϵ 12 000), 260 (8000), 272 (sh) nm (6500); ¹H NMR δ (CDCl₃)¹⁰ 2.76 (tt, 4 H, $J_1 = 6.0$, $J_2 = 1.0$ Hz, H₆, H_{6'}, H₁₄, H_{14'}), 5.53 (td, 4 H, $J_1 = 12.0$, $J_2 = 6.0$ Hz, H₅, H₇, H₁₃, H₁₅), 6.17 (td, 4 H, $J_1 = 12.0$, $J_2 = 1.0$ Hz, H₄, H₈, H₁₂, H₁₆), 6.85–7.20 ppm (m, 6 H aromatic). Irradiation at 2.76 ppm rendered the vinylic spectrum into a simple AB pattern. The NMR spectrum confirms a *cis* configuration for the double bonds ($J = 12.0$ Hz). It should be noted that the pattern of both the vinylic protons and of H₆, H_{6'}, H₁₄, and H_{14'} are very similar to that of dibenzo[*a,c*]cyclononatetraene.¹¹ Even a tenfold excess of the phosphonium salt and base did not enable the direct synthesis of **4** from biphenyl-2,2':6,6'-tetracarboxaldehyde.⁷ Treatment of **4** with *n*-BuLi in THF-*d*₈ produced a deep red solution with the following ¹H NMR spectrum:¹⁰ δ 2.92 (t, 2 H, $J = 7.0$ Hz, H₆, H₁₄), 4.62 (d, 4 H, $J = 12$ Hz, H₄, H₈, H₁₂, H₁₆), 5.86 (t, 4 H, $J_1 = J_2 = 7.0$ Hz, H₅, H₇, H₁₃, H₁₅), 6.80 (m, 2 H, aromatic), 7.08 ppm (m, 4 H, aromatic). We attribute this spectrum to a nonplanar, partially delocalized structure, **5**. A similar phenomenon has been observed upon deprotonation of dibenzo[*a,c*]cyclononatetraene.^{11a} After some time at room temperature, the ¹H NMR spectrum of **5** disappeared; a new spectrum was concomitantly observed (the half life time of **5** is ca. 5 h). The following ¹H NMR spectrum was observed:¹⁰ δ 6.35 (t, 2 H, $J = 4.0$ Hz, H₆, H₁₄), 6.67 (d, 4 H, $J = 5.0$ Hz, H₄, H₈, H₁₂,

H₁₆), 7.01 (t, 4 H, $J = 5.0$ Hz, H₅, H₇, H₁₃, H₁₅), 7.20 (t, 2 H, $J = 8.0$ Hz, H₂, H₁₀), 8.35 ppm (d, 4 H, $J = 8.0$ Hz, H₁, H₃, H₉, H₁₁). This spectrum is assigned to the planar delocalized anion **1**. In spite of the formation of two negative charges, a downfield shift is observed in **1** relative to **5**. The chemical shift difference $\Delta\delta_{5 \rightarrow 1}$ is 3.4, 2.0, and 1.25 ppm for H₆, H₁₄; H₅, H₇, H₁₃, H₁₅; and H₄, H₈, H₁₂, H₁₆, respectively. This downfield shift is attributed to the formation of a planar delocalized system. The absorption at 8.35 ppm is due to the proximity of H₄, H₈, H₁₂, and H₁₆ of the planar nine-membered-ring system to the benzene moiety. The vicinal (ortho) coupling constants in **1** ($J = 5.0$ and 4.0 Hz) in contrast to the corresponding coupling constants of the partially delocalized dianion **5** ($J = 12.0$ and 6.0 Hz) indicates the formation of a planar aromatic dianion. Quenching of **1** or **5** produces a mixture of **4** and other allyl isomers.¹²

From all the above, it may be concluded that dibenzo[*gh,op*]nonalene dianion (**1**) is a planar, delocalized diatropic dianion with a peripheral diamagnetic ring current. It is the first system to have been derived from the hitherto unknown nonalene skeleton.

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References and Notes

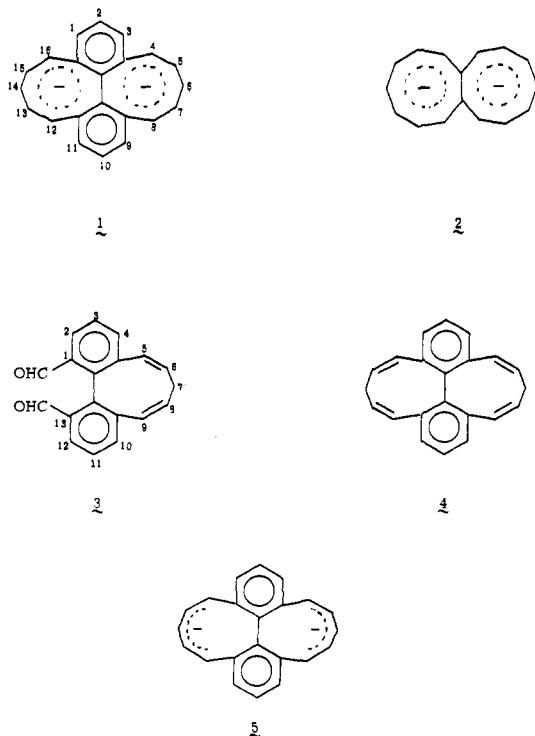
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- (8) S. C. Agrawal and B. L. Van Duuren, *J. Org. Chem.*, **40**, 2307 (1975).
- (9) All new compounds showed correct C, H analyses.
- (10) Proton spectra are reported in parts per million downfield from Me₄Si. The spectra were recorded on a HA-100D spectrometer, probe temperature 31 °C. Additional support for the assignments came from the results of double resonance experiments carried out with a Hewlett-Packard 4204A oscillator.
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- (12) Quenching of **1** or **5** with water resulted in the protonation of positions 4, 6, 8, 12, 14, and 16 (which correspond to positions with the highest charge densities according to HMO calculations). In the product mixture, **4** was identified in ~30% yield (NMR). The other isolated (PLC) quenching products (~45%) were identified as allyl isomers of **4** by catalytic hydrogenations and comparison with the hydrogenation product of authentic **4** (NMR, mass spectrum).

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Studies of Individual Methine Aromatic Carbon Sites of Proteins by Natural-Abundance Carbon-13 Nuclear Magnetic Resonance Spectroscopy at High Magnetic Field Strengths

Sir:

Natural-abundance ¹³C Fourier transform NMR spectra of small globular proteins have yielded numerous narrow individual-carbon¹ resonances of nonprotonated aromatic carbons (Figure 1), even at magnetic field strengths as low as 14