

2-Methylenebicyclo[3,2,1]octa-3,6-diene, a Bishomofulvene-type Structure

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Summary From a study of its n.m.r. and u.v. spectra and its dipole moment, it has been shown that the resonance contribution of a bishomofulvene-type structure is important in 2-methylenebicyclo[3,2,1]octa-3,6-diene (**2**).

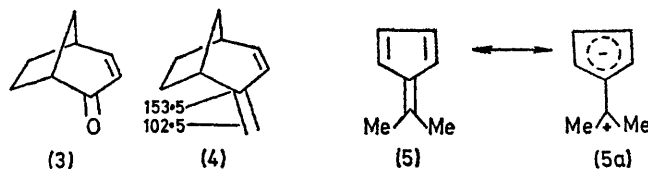
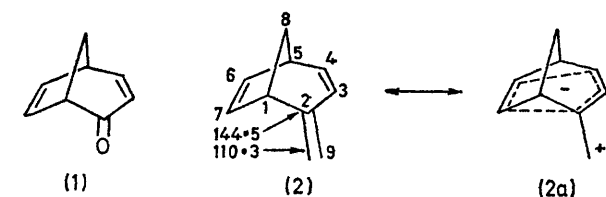
WE report the syntheses and properties of 2-methylenebicyclo[3,2,1]octa-3,6-diene (**2**) and 2-methylenebicyclo-

[3,2,1]oct-3-ene (**4**). The olefin (**2**) was obtained in good yield either from the reaction of (**1**)¹ with triphenylphosphine methylide in THF or from the addition of methylmagnesium iodide to (**1**) followed by dehydration of the resulting methylcarbinol. The structure of (**2**) followed from its ¹H n.m.r.‡ [τ 3.60—4.20 (4H), 4.95 (1H, m), 5.19 (1H, m), 6.71 (1H, m), 7.18 (1H, m), and 7.85 (2H, m)] and mass

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‡ Detailed analysis of ¹H and ¹³C n.m.r. spectra will be reported in a forthcoming full paper.

spectra. The latter spectrum confirmed the molecular weight (118) and the base peak was attributed to $(M - 1)^+$,



(6)

corresponding to $C_9H_9^+$. Compound (4) was similarly prepared from (3)² τ 4.20 (2H, m), 5.20 (2H, m), and 7.5—8.5 (8H, m)].

The most striking physical properties of (2) are its ^{13}C n.m.r. and u.v. spectra and its dipole moment.³

The ^{13}C n.m.r. chemical shifts of C-2 and C-9 in (2) are δ (Me₄Si) 144.5 and 110.3, respectively. Under identical conditions, the ^{13}C n.m.r. chemical shifts of C-2 and C-9 in (4) are δ (Me₄Si) 153.5 and 102.5, respectively, *i.e.*, it could be taken that the C-2 in (2) is more electronegative than that in (4) and the C-9 in (2) is more positive than that in (4).⁴ This suggests that resonance contribution of (2a) is important in (2).

Measurement of the u.v. spectrum of (2) showed a broad absorption having fine structure at 243 nm (ϵ 12,000) (calculated⁵ λ_{max} 232 nm). The olefin (4) has a spectrum with λ_{max} at 230 nm, and ϵ_{max} 5000. This bathochromic effect of 13 nm in (2) can be accounted for in a similar manner [*cf.* (5) \longleftrightarrow (5a)].

The dipole moment was found to be 0.59 D, which suggests a high degree of charge separation in (2).[§]

These data for (2) are in accord with a delocalized bishomofulvene-type resonance structure (2a).⁶

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[§] The dipole moment was determined by measuring the dielectric constants and densities of solutions of varying molarity at 20° in benzene and extrapolating.

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³ The same treatment has previously been applied to methylenenorbornadiene and methylenebicyclo[4,2,1]nona-2,4,7-triene; R. W. Hoffmann, R. Schuttler, W. Schafer, and A. Schweig, *Angew. Chem. Internat. Edn.*, 1972, 11, 512; M. T. Reetz, R. W. Hoffmann, W. Schafer, and A. Schweig, *ibid.*, 1973, 12, 81.

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⁶ For a homoaromatic bishomocyclopentadienide anion (6), see J. M. Brown and J. L. Occolowitz, *Chem. Comm.*, 1965, 376; S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, 1967, 89, 3656.