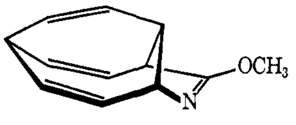
49-50°;[5] $\nu_{max}^{CHCl_3}$ 1634 cm^{-1}; uv (C_2H_5OH): shoulder at 245 nm (ε 165)] was obtained in 78% yield.



9

Although these 1,2 and 1,6 additions to bullvalene can be satisfactorily represented by collapse of **2** *via* four- and five-centered transition states, a modification which includes concerted or nearly concerted addition of CSI to **1** and irreversible passage of **3a** to **2** cannot yet be excluded. Also, questions concerning the precise electronic character of the cationic moiety in **2** remain open and await answers which we hope to provide in due course.

Acknowledgment. We wish to thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene which made this study possible.

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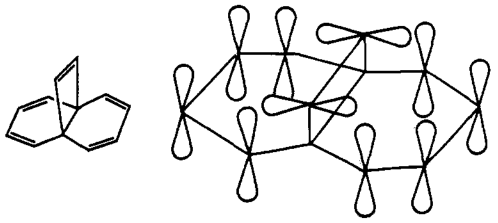
[4.4.2]Propella-2,4,7,9,11-pentaene[1]

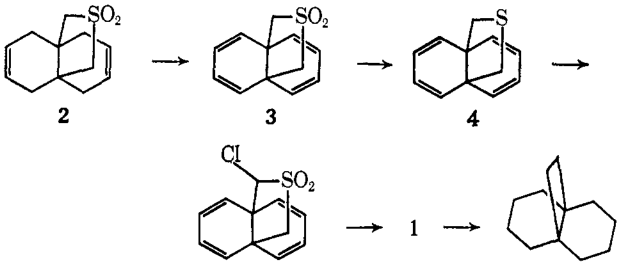
Sir:

An awareness that the interrelationship between electronic interaction and the presence or absence of thermodynamic stabilization is a function of the geometry of orbital overlap (neutral molecules) and the sum and distribution of π electrons (charged species) has developed appreciably in recent years. For example, it is now clear that, whereas alignment of the terminal p orbitals of hexatriene within orbital overlap as in benzene produces aromatic stabilization, similar arrangement of the p orbitals of butadiene as in cyclobutadiene results in loss of delocalization energy.[2] Placement of three ethylenic moieties in a cylindrical array as in barrelene results in no obvious delocalization;[3] in contrast, the bicycloheptadien-7-yl cation is decidedly stabilized and bicycloaromatic.[4] To the present time, barrelene represents the only polyene with $(4n + 2)$ p electrons arranged for orthogonal (or nearly orthogonal) interaction. We wish now to describe the synthesis and properties of [4.4.2]propella-2,4,7,9,11-pentaene (**1**), a system in which orthogonal overlap of two cyclobutene p orbitals with terminal p lobes of two cyclohexadiene units makes possible a unique form of interaction of ten π electrons along the top surface of the hydrocarbon.



1

Dibromination of 12-thia[4.4.3]propella-3,8-diene 12,12-dioxide (**2**),[5] followed by direct dehydrobromination of the unpurified tetrabromide with sodium methoxide in refluxing anhydrous tetrahydrofuran, gave sulfone **3**, mp 160-162°,[6] in 45% yield; $\delta_{TMS}^{CDCl_3}$ 3.36 (singlet, 4 H, $-CH_2SO_2-$) and 5.82 (center of A_2B_2 pattern, 8 H, vinyl protons). Reduction of **3** with ethereal lithium aluminum hydride proceeded readily to give **4** in quantitative yield. This sulfide was chlorinated directly with N-chlorosuccinimide and oxidized with monoperphthalic acid, thus affording the critical α-chloro sulfone intermediate **5**, mp 151-153°,[6] in 42% over-all yield from **3**; $\delta_{TMS}^{CDCl_3}$ 5.14-6.47 (complex multiplet including sharp singlet at 5.29, 9 H, vinyl protons, and $-CHClSO_2-$), 3.56 and 3.30 (AB pair, J = 13 Hz, 2 H, $-CH_2SO_2-$). Exposure of **5** to a slurry of powdered potassium *t*-butoxide in anhydrous ether at ambient temperature for 4 hr resulted in smooth conversion to **1** which was purified by preparative vapor-phase chromatography at 110° (10% SE-30 on Chromosorb G, 14% isolated yield).[6,7] Hydrogenation of the colorless oil in methanol over 10% palladium on carbon proceeded with the constant uptake of 5 equiv of hydrogen and formation of previously characterized [4.4.2]propellane (**6**).[5,8]



The nmr spectrum of **1** demonstrated the presence of two cyclobutene (singlet, δ 5.90) and eight other vinyl protons (A_2B_2 pattern, δ 5.68). Its ultraviolet spectrum in isooctane displayed two maxima at 247 nm (ε 2500) and 290 nm (ε 2100). These spectral properties compare favorably with those of related cyclohexadienes (Table I) and support the conclusion that **1** is polyolefinic in nature.[9]

The cleavage of **1** into naphthalene and acetylene involves a $({}_\sigma 2_s + {}_\sigma 2_s)$ bond cleavage which on the basis of orbital symmetry considerations[10] is not likely to proceed thermally in concerted fashion. In actual fact, [4.4.2]propella-2,4,7,9,11-pentaene exhibited pronounced thermal stability as evidenced by essentially quantitative recovery from a gas chromatographic column maintained at 120° (residence time, 20 min).

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[1] α-Halo Sulfones. XIV. Part XIII is L. A. Paquette and J. C. Philips, *Chem. Commun.*, in press.

[2] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 3255 (1965), and pertinent references cited therein.

[3] H. E. Zimmerman and R. M. Paufler, *ibid.*, **82**, 1514 (1960); H. E. Zimmerman and G. L. Grunewald, *ibid.*, **86**, 1434 (1964); C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *ibid.*, **82**, 5450 (1960).

[4] M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

[5] L. A. Paquette and J. C. Philips, *Tetrahedron Letters*, 4645 (1967).

[6] All new compounds cited herein gave acceptable (±0.3%) combustion analysis values.

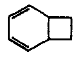
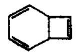
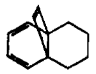
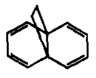
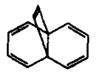
[7] Calcd: m/e 154.0782. Found: m/e 154.0776.

[8] (a) E. Vogel, W. Maier, and J. Eimer, *Tetrahedron Letters*, 655 (1966); (b) J. J. Bloomfield and J. R. S. Irelan, *ibid.*, 2971 (1966); (c) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron Suppl.*, **8**, 279 (1967).

[9] It is interesting to note, however, that the 290-nm band of **1** represents the longest wavelength absorption band yet reported for a cyclohexadienyl system.

[10] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

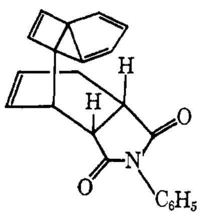
Table I. Ultraviolet and Chemical Shift Data for Selected 1,3-Cyclohexadienes

Compound	λ_{max} (ϵ)	Solvent	Olefinic protons (δ)	Pattern	Ref
	274 (3340)	Cyclohexane	5.62	Multiplet	*a*
	273 (3100) 277 (3000)	(unspecified)	5.63	Multiplet	*b*
	268 (2400) 276 (sl infl, 2100)	Isooctane	5.53	A_2B_2	*c*
	235 (4700) 285 (2600)	Cyclohexane	5.50	A_2B_2	*d*
	247 (2500) 290 (2100)	Isooctane	5.68	A_2B_2	*e*

[a] A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **80**, 5505 (1958). [b] E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **3**, 442 (1964). [c] Reference 1. [d] References **8a** and **8b**. [e] This work.

The even number of suprafacial components required for fragmentation of **1** to naphthalene and acetylene suggests photochemical allowedness; in agreement with theory, photoexcitation of **1** with 2537-Å radiation resulted in rapid formation of the above-mentioned retrograde products.

Admixture of equimolar amounts of **1** and N-phenylmaleimide in benzene solution at room temperature resulted in the gradual deposition of colorless crystals of (4 + 2)π adduct **7** (94%), mp 277–279°.[6] The stereochemistry of this cycloaddition product has been assigned in accordance with the observed vicinal proton coupling constant and established precedence.



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In light of these limited observations, it would appear that orbital overlap of ten π electrons in the unusual fashion enforced by the inflexibility of pentaene **1** results in little or no enhancement of thermodynamic stabilization. Nevertheless, the ready availability of hydrocarbon **1** now makes possible the opportunity to examine the effect of such an arrangement of π-atomic orbitals on chemical reactivity, a point on which we hope to report further at a later date.

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(11) National Institutes of Health Predoctoral Fellow, 1966–1968.

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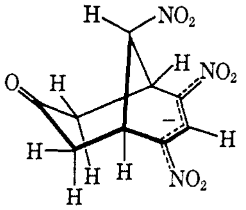
Condensation of Acetone with *sym*-Trinitrobenzene. Structure of the Bicyclic Product

Sir:

Attempts to clarify the complex reaction of acetone with *sym*-trinitrobenzene and diethylamine have been made by a number of workers.[1-5] N,N-Diethyl-*p*-nitroaniline and 2-acetonyl-1,3-dinitropropane have been identified as products.[1] In addition, an unknown red compound has been isolated from the reaction mixture.[1,3] This material has an intense absorption at 510 mμ and is similar to the red product isolated by Abe[4] from a mixture of *sym*-trinitrobenzene, acetone, and aqueous ammonia. On the basis of an elemental analysis of the red product prepared using diethylamine, Osugi and Muneo[3] proposed a structure containing acetone, *sym*-trinitrobenzene, and amine in a molar ratio of 1:1:2. The elemental analysis reported by Foster and Fyfe[1] is not consistent with this stoichiometry or with a 1:1:1 adduct. A crystalline sample was not obtained, however.

We have isolated the red compound by Foster and Fyfe's method and after recrystallization from chloroform obtained red crystals, mp 171–172°, $\lambda_{max}^{100\%\ EtOH}$ mμ (ϵ): 510 (30,300). The elemental analysis and nmr spectrum (acetone-d_6), Figure 1, are consistent with **1**. A 1:1:1 adduct ($C_{13}H_{20}N_4O_6$) requires C, 45.35; H, 5.85; N, 16.27. Found: C, 45.40; H, 5.78, N, 16.25. The proton on the dinitropropenide portion of **1** appears as a singlet at δ 8.52 (1 H). The N-H protons appear as a broad singlet at δ 6.84 (2 H). The bridge H-CNO_2 proton appears as a triplet centered at δ 5.72, *J* = 3 cps (1 H). The appearance of this proton 1.3 ppm downfield from the absorption observed for a dilute solution of nitromethane in acetone (δ 4.4) and 1.0 ppm downfield from the methine proton of 2-nitropropane leads us to believe that the nitro group on the one-carbon bridge is directed toward the anionic portion of the molecule. If it were not, the bridge proton would occupy a position directly above the delocalized system, a region of high shielding, and would be expected to appear at higher fields than in normal aliphatic nitro compounds. In addition, if the bridge proton is directed toward the carbonyl function it would lie in a deshielding region (assuming conformational mobility of the keto bridge). The coupling constant of 3 cps is consistent with a dihedral angle of 50° between the bridging and bridgehead protons,[6] a value in accord with models of **1**, and the coupling observed in related bicyclic systems.[7] The two bridgehead protons appear



, $H_2\overset{+}{N}(CH_2CH_3)_2$

1

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(1) R. Foster and C. A. Fyfe, *Tetrahedron*, **22**, 1831 (1962).
(2) Penkett, Thesis, University of Leeds, 1963.
(3) J. Osugi and Muneo, *Rev. Phys. Chem. Japan*, **37**, 43 (1967).
(4) T. Abe, *Bull. Chem. Soc. Japan*, **32**, 997 (1959).
(5) C. R. Allen, A. J. Brook, and E. F. Caldin, *J. Chem. Soc.*, 2171 (1961).
(6) H. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).