the presence of excess RNC, the two terminal CO ligands are also replaced yielding $[Rh_2(\mu\text{-}CNR)(CNR)_2(dpm)_2]$ which is isoelectronic with the Pd dication $[Pd_2(\mu\text{-}CNR)(CNR)_2(dpm)_2]^{2+}$ reported by Balch.[2]

We have thus shown that complex I provides a useful entry into the synthesis of A-frame complexes, and that some of these resultant species exhibit significant catalytic activity in the shift reaction and acetylene hydrogenation.

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(9) Elemental analysis for **1** is satisfactory. Calcd for $C_{52}H_{44}P_4O_2Rh_2$: C, 60.60; H, 4.30; P, 12.02. Found: C, 60.25; H, 4.69; P, 11.57. The $^{31}P\{^1H\}$ NMR spectrum for **1** shows a symmetric multiplet centered at δ 29.51 relative to $OP(OMe)_3$ with four principal lines. This pattern which is not unambiguously interpretable differs from those found for A-frame type complexes with bridgehead ligands in which the mirror symmetric spectrum shows only two principal lines. The ^1H spectrum shows in addition to the phenyl protons only one broad resonance at δ 4.32 for the $-CH_2-$ protons of the dpm ligand. The isomer of **1** obtained by the reaction of $RhH(CO)(PPh_3)_3$ with dpm appears in solution to be $Rh_2(\mu\text{-}CO)(CO)(dpm)_2(PPh_3)$ by an IR spectrum showing terminal and briding ν_{CO} at 1915 and 1800 cm^{-1}, and by the identity of the IR and NMR spectra for this system with those obtained by adding PPh_3 to a solution of 1. Upon isolation, however, this "isomer" appears to lose PPh_3 and is consistent with analytical data for $[Rh_2(CO)_2(dpm)_2(solvent)]$. A key feature of the characterization of 1 and its isomer is that in all of their reactions identical products are obtained.
(10) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The programs and procedures are similar to those reported previously by Goldberg, S. Z.; Kubiak, C.; Meyer, C. D.; Eisenberg, R. *Inorg. Chem.* **1975,** *14,* 1650.
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(22) Complex **5** in C_6H_6 solution shows ν_{CO} at 1946 (s, sh) and 1938 (vs) cm^{-1}. The ^1H NMR spectrum shows dpm $-CH_2-$ resonances at δ 3.35 and 2.91 (m), similar to that found in many A-frame complexes. The $^{31}P\{^1H\}$ spectrum shows a symmetric multiplet centered at δ 17.66 with two intense principal lines separated by 133.0 Hz. The spectrum is qualitatively similar to that for **3.** The phenylacetylene complex analyzes for a solvated species $[Rh_2(CO)_2(PhCCH)(dpm)_2]\cdot$solvent and shows ν_{CO} at 1958 (vs) and 1930 (s) cm^{-1}. The ^1H NMR spectrum shows dpm $-CH_2-$ resonances at δ 3.77 and 2.89, while the $^{31}P\{^1H\}$ spectrum lacks the symmetry of other A-frame systems as would be expected for acetylene binding in the manner recently described by Balch[23] for $CF_3C{\equiv}CCF_3$ addition to $Pd_2Cl_2(dpm)_2$.
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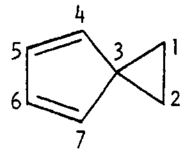
Microwave Spectrum, Dipole Moment, and Structure of Spiro[2.4]hepta-4,6-diene. Evidence for Significant Cyclopropyl Conjugation

Sir:

The question of whether the cyclopropyl ring is able to conjugate with adjacent unsaturated π systems has been one of long-standing interest. One fundamental measure of such an interaction is that of molecular structure. The matter has been discussed theoretically by Hoffmann[1] who pointed out that electron donation from the highest occupied molecular orbital (HOMO) of cyclopropane (3e′) to the lowest unoccupied molecular orbital (LUMO) of a π system should lead to predictable changes in structural parameters. One of the best documented cases is that of cyclopropyl cyanide, for which the C_1–C_2 bond is 0.028 Å longer than the C_2–C_3 bond,[2] in accord with theoretical expectations. Recent high-quality ab initio calculations[3] for this molecule are in complete agreement with the experimental findings.

Spiro[2.4]hepta-4,6-diene (**1**) is a molecule for which such π conjugation might be expected to have significant structural consequences. Conjugation (π delocalization) in molecules of this type has been discussed theoretically by Gleiter et al.[4] and by Kao and Radom.[5] Experimental PES[4] and NMR measurements[6] support the view that significant π conjugation occurs. On the other hand, electron diffraction (ED) structural results[7] showed the spiroheptadiene bond lengths to be essentially the same as in the parent cyclopropane and cyclopentadiene moieties. Because of previous difficulties[8] in the unambiguous ED determination of bond lengths in hydrocarbons containing several similar but nonidentical C-C bonds, we have undertaken a microwave spectroscopic investigation of **1**.



1

The microwave spectrum was remarkably intense, and consisted of easily assignable *a*-type R-branch transitions characteristic of a near-prolate asymmetric rotor. A total of 52 transitions, including a few high-*J* Q-branch lines, were analyzed to obtain the rotational constants of the normal isotopic species given in Table I. The complete set of measured lines is available in a supplementary microfilm table. Intensity

Table I. Rotational Constants and Moments of Inertia of the Normal Isotopic Species of Spiro[2.4]hepta-4,6-diene

A	6102.149 ± 0.014^a	I_a	82.81984^b
B	2454.223 ± 0.001	I_b	205.9222
C	2028.890 ± 0.001	I_c	249.0914

[a] Units are MHz, uncertainties are one standard deviation. [b] Units are amu Å^2, computed using the factor 505 379.

Table II. Dipole Moment Measurements

transition	M	$(\Delta\nu/E^2) \times 10^5$ obsd[a]	$(\Delta\nu/E^2) \times 10^5$ calcd[a]
$5_{23} \rightarrow 6_{24}$	2	−0.2436	−0.2431
$5_{23} \rightarrow 6_{24}$	1	−0.0644	−0.0637
$5_{24} \rightarrow 6_{25}$	2	0.2462	0.2468
$5_{24} \rightarrow 6_{25}$	1	0.0587	0.0586
$\mu_T = \mu_a = 0.947 \pm 0.003^b$			

[a] Units are MHz/(V/cm)^2. [b] Uncertainty represents 3σ.

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Table III. Structural Parameters of Spiro[2.4]hepta-4,6-diene and Related Molecules

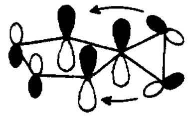
parameter[a]	cyclopropane ED[b]	cyclopentadiene mw[c]	fulvene mw[d]	spiro[2.4]hepta-4,6-diene mw[e]	ED[f]	STO-3G[g]
C_1C_2	1.510			1.494	1.510	1.495
C_2C_3	1.510			1.546	1.510	1.518
C_3C_4		1.506	1.468	1.462	1.509	1.506
C_4C_5		1.344	1.357	1.361	1.341	1.321
C_5C_6		1.468	1.476	1.467	1.460	1.488
μ		0.42	0.42	0.95		0.58

[a] Distances are in ångstroms and dipole moments in debyes. All rings have been numbered to correspond to **1**. [b] Electron diffraction.[12] [c] Microwave.[10] [d] Microwave.[11] [e] This work. [f] Electron diffraction.[7] [g] Reference 5.

variations arising from the nuclear statistical weights of the equivalent protons were in complete accord with C_{2v} molecular symmetry.

The dipole moment has been determined by performing standard second-order Stark effect measurements,[9] the results of which are summarized in Table II. The resulting moment, $\mu = 0.947 \pm 0.003$ D, is one of the largest values known to us for any hydrocarbon, and is considerably larger than the value of 0.42 D for cyclopentadiene[10] and fulvene.[11] Hybridization changes undoubtedly contribute to the electric dipole moment resulting by fusion of polar cyclopentadiene with nonpolar cyclopropane to form spiroheptadiene, but the especially large moment suggests that the HOMO → LUMO interaction (**2**) plays an important role.

To obtain further information about the role of conjugation, we have determined the molecular structure by performing microwave studies of ^{2}H-labeled and ^{13}C isotopic species. The spectral analysis and structure will be reported in detail at a later time, but we have summarized our initial results for the C-C bond distances in Table III along with other relevant structural data. The microwave distances, obtained by studying all of the natural abundance monosubstituted ^{13}C species, differ substantially from the previous ED values;[7] moreover, the bond lengths show substantial variations from those of the parent cyclopropane[12] and cyclopentadiene[10] molecules. On referring to the HOMO → LUMO orbital interaction diagram **2**, it is seen that all of the spiroheptadiene bond lengths have changed in the direction predicted by this model.



2

Finally, we observe that the published geometry-optimized STO-3G calculations[5] fail to yield an accurate structure, which leads in turn to a poor value of the dipole moment. We have performed STO-3G calculations[13] using the microwave structure, and find a dipole moment of 0.90 D, in good agreement with experiment. These computations show also the expected net shift of electrons out of the cyclopropyl ring into the cyclopentadiene ring as shown in Figure 1. (Note that STO-3G calculations show that the π orbitals of cyclopropane of geometry **1** have charges of -0.071 at C_1 and -0.104 at C_3.)

In summary, experimental dipole moment and structural data strongly support significant conjugation of the cyclopropyl ring with the diene unit in spiroheptadiene. Moreover, ab initio calculations performed with the correct experimental geometry yield entirely supportive results.

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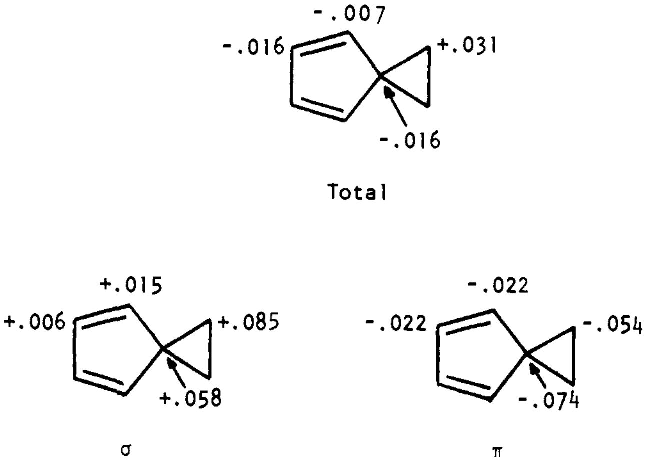

Figure 1. Total, σ, and π charges of **1** from STO-3G calculations and the microwave structure reported in this study. The total and σ charges refer to the CH_2 units at C_1 and C_2 and to the CH units at C_4–C_7.

Supplementary Material Available: Table S-I, a listing of all measured spectral lines for the ground vibrational state of spiro[2.4]-hepta-4,6-diene (1 page). Ordering information is given on any current masthead page.

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