periodic table are rare. It has been established that the carbonate, nitrate, acetate, and nitrite ions function as bidentate chelates in the octahedral systems, $[Co(NH_3)_4CO_3]^+$,[8] $[Co(Me_3PO)_2(NO_3)_2]$,[9] zinc acetate dihydrate,[10] and $[Ni(Me_2N(CH_2)_2NMe_2)(NO_2)_2]$,[11] respectively. The cobalt(III) derivative of 1,3-diphenyltriazene appears to provide the first proven example where three four-membered rings are present in the one octahedral coordination sphere.

Acknowledgment. We are very grateful to Dr. J. C. B. White for allowing us to use his computer programs.

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On the Thermodynamic Significance of Delocalization in Dienes. Thermodynamics of the Vinylcyclopropyl System

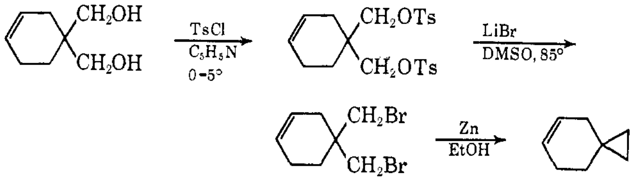
Sir:

It has long been known from thermochemical evidence that the heats of formation (ΔH_f) of conjugated[1] compounds, such as dienes, are significantly lower (more stable) than the sum of bond energy terms obtained from saturated or monoolefinic models. The relative importance of the factors contributing to this stabilization (which is generally referred to as the empirical resonance energy) is not clear and has been the subject of considerable discussion in recent years. The commonly accepted interpretation[2] holds that π delocalization or resonance accounts for a major portion of this energy difference; more recently, the view[3] has been advanced that delocalization may be relatively unimportant in the ground state of "classical" molecules[4] and that the energy differences can be accounted for on the basis of variations in the binding energy of σ bonds as a function of hybridization.

In the absence of a complete and accurate mathematical description of complex molecules, concepts such as hybridization and delocalization can be very useful from a predictive standpoint. In order to clarify the relative thermodynamic importance of these concepts, we have determined the empirical resonance energy of the vinylcyclopropyl system and evaluated it with respect to the known empirical resonance energy of 1,3-butadiene.[5,6]

Interaction of the cyclopropyl group with conjugated π systems has been a subject of continuing interest.[7] Recently the geometric consequences of such interactions have been elucidated by nmr,[8] electron diffraction,[9] and kinetic[10] studies. These studies have conclusively established that the minimum energy conformation possesses a "bisected" geometry[11] in which the nodal plane of the adjacent π system is normal to the plane of the ring, thus allowing maximum delocalization between the π system and the highly p weighted bonds of the cyclopropyl ring. However, although approximate conformational energy differences have been obtained for vinylcyclopropane and closely related compounds,[8a,c-f] and thermochemical studies have been reported for phenyl- and vinylcyclopropane,[7c,12,13] the thermodynamic significance of ground-state interactions in these compounds remains problematical.

We have synthesized spiro[2.5]oct-5-ene (**1**) by the following scheme[14] and have equilibrated both **1** and its conjugated isomer **2**[15] in solutions of *ca.* 1 *N* lithium dimethylamide in hexamethylphosphoramide[16] (LDMA-HMPA) at three different temperatures (see Table I). Equilibrium mixtures were usually obtained in less than 10 min with essentially no decom-



1 2

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[1] The term conjugated is used here only to refer to the structural feature of alternating single and double bonds (or cyclopropyl rings).

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[4] Classical molecules have been defined as those for which only a single unexcited resonance structure can be written.[3a]

[5] This is calculated to be 3.95 kcal/mole from the heats of formation [$\Delta H_{f,298}(l)$] of butane, 1-butene, and 1,3-butadiene: "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, Part 5, 1960.

[6] For a discussion of a calculation of this quantity, as well as its implications, see L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 101–105.

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[9] (a) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965); (b) L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

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[12] M. P. Kozina, M. Yu Lukina, N. D. Zubareva, I. L. Safonova, S. M. Skuratov, and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR*, **138**, 843 (1961). The heat of combustion of phenylcyclopropane reported by these workers differs from the value reported in ref 7c by 1.3 kcal/mole.

[13] The apparent negative resonance energy reported for vinylcyclopropane[7c] is probably not real in light of our present results. Partial polymerization of the combustion sample in transit cannot be discounted: E. J. Prosen, private communication.

[14] (a) This is similar to the scheme of P. Leriverend and J. M. Conia, *Bull. Soc. Chim. France*, 116, 121 (1966). (b) The bromination step is a modification of the procedure of J. Cason and J. S. Correia, *J. Org. Chem.*, **26**, 3645 (1961). All new compounds have been fully characterized by their nmr, infrared, and (for **2**) ultraviolet spectra. Satisfactory analyses were obtained in all cases.

[15] This compound has recently been reported by M. Hanack, *Angew. Chem. Intern. Ed. Engl.*, **4**, 603 (1965); W. Kirmse and K. H. Pook, *ibid.*, **5**, 594 (1966).

[16] A. Schriesheim, C. A. Rowe, Jr., and W. Bartok, Belgian Patent 617,842 (1963); *Chem. Abstr.*, **59**, 3772 (1963).

Table I. Equilibrium Constants (K_{eq}) and Free Energies of Isomerization (ΔF_{isom}) for the Equilibrium **1** $\rightleftarrows$ **2**

Temp, °C	K_{eq}	ΔF_{isom}, kcal/mole
0.0	7.45	-1.09 ± 0.03
25.0	6.26	-1.09 ± 0.03
50.0	5.48	-1.09 ± 0.03

position and were analyzed by gas chromatography[17] using a 4-m column of Carbowax 1000 on 70–80 mesh silanized Chromosorb P.

The conformation of **2** is such that the cyclopropyl ring is fixed in its minimum energy conformation with respect to the double bond, thus effecting a maximum contribution due to delocalization. From the above data, this isomer has (from a least-squares evaluation) a lower heat of formation [$\Delta H_{f,298}$(l)] of 1.08 ± 0.07 kcal/mole in LDMA–HMPA solution than does the nonconjugated isomer **1**.

The important consideration is the amount of stabilization *in terms of chemical binding energy* which is a consequence of the structural feature of conjugation in **2** relative to **1**. In order to determine this, other terms contributing to $\Delta H_{f,298}$(l) must be estimated and eliminated. These include terms due to conformational, intermolecular interaction, kinetic, and zero-point energy differences.

Differences between structurally similar compounds due to the last three factors are generally considered to be minimal.[18,19] The one conformational energy term for which a correction may be needed is due to differences in torsional strain. We estimate that **2** possesses, if any, not more than *ca.* 0.2 kcal/mole more torsional strain than **1**.[20] Thus the chemical binding energy of **2** is estimated to be 1.1 to 1.3 kcal/mole greater than that of **1**.

Although it is difficult to estimate the contribution of delocalization to the above corrected empirical resonance energy, these results are relevant to the problem of the delocalization energy of 1,3-butadiene. Our approach is to arbitrarily ascribe all of the corrected empirical resonance energy of the vinylcyclopropyl system to hybridization effects and to correct for estimated hybridization differences between this system and 1,3-butadiene, thereby estimating the *maximum* contribution of hybridization effects in the diene system. Taking the exocyclic orbitals of the cyclopropyl ring to have 31% s character[21] and using "hybridization ratios"[2a] calculated from the bond angles in cyclohexane,[22] 1,3-butadiene,[23] propene,[24] and butane,[25] one can, using the bond energy scheme of Cox[26] (which assumes that all carbon–carbon single bond energy differences are due to hybridization), assign a *maximum* contribution of 1.7 kcal/mole to the empirical resonance energy of 1,3-butadiene due to hybridization effects. This, therefore, indicates that delocalization contributes a *minimum* of 1.9 kcal/mole to the corrected empirical resonance energy (3.6 kcal/mole)[19] of 1,3-butadiene.[27] This figure will be larger by at least the amount which delocalization contributes to the empirical resonance energy of the vinylcyclopropyl system.

Acknowledgment. We are pleased to acknowledge the support of this work by the Maryland General Research Board and the Petroleum Research Fund of the American Chemical Society.

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[17] Relative peak areas were calibrated using known mixtures.

[18] (a) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth & Co. (Publishers) Ltd., London, 1958, p 104; (b) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p 76.

[19] Correction for these terms *reduces* the empirical resonance energy of 1,3-butadiene[5] by less than 10% (to 3.6 kcal/mole). This latter quantity is ΔH_0(g) minus the zero-point energy contributions. The zero-point energies of butane and 1-butene [T. L. Cottrell, *J. Chem. Soc.*, 1448 (1948)] were used along with the zero-point energy for 1,3-butadiene calculated from the frequency assignments reported by R. K. Harris, *Spectrochim. Acta*, 20, 1129 (1964).

[20] The minimum torsional strains were carefully estimated with the use of Dreiding models. The vinylcyclopropyl barrier was taken to be 2.5 kcal/mole[9] and the interorbital angle for cyclopropane was taken to be 100° [C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 27 (1966)].

[21] This value corresponds to $\angle \mathrm{CCC} = 116.7^\circ$ (in the cyclohexene ring), which is intermediate between $\angle \mathrm{HCH} = 120^\circ$ for cyclopropane [H. H. Gunthard, R. C. Lord, and T. K. McCubbin, Jr., *J. Chem. Phys.*, **25**, 768 (1956)] and $\angle \mathrm{CCC} = 111.55^\circ$ in cyclohexane.[22] It is weighted toward the cyclopropane value because of the flexibility of the cyclohexene part of the spiran system and is probably a low estimate.

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[23] A. Almenningen, O. Bastiansen, and M. Traetteberg, *ibid.*, **12**, 1221 (1958).

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[26] J. D. Cox, *Tetrahedron*, **19**, 1175 (1963); **18**, 1337 (1962). The hybridization values used by Cox were modified to correspond to the bond angles in the model compounds.

[27] Recent calculations suggest a significant delocalization energy for 1,3-butadiene [0.2047 ev: M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 692 (1965)], although this value is thought to be too high: M. J. S. Dewar, private communication.

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Inversion during the Addition of Amino Acids to the D-*cis*-α-[Co(L,L-α,α'-dimethyltrien)Cl_2]$^+$ Ion

Sir:

An important approach to elucidating reaction mechanisms is through the study of stereochemistry. J. C. Bailar and his co-workers have pioneered the use of this approach in inorganic chemistry through their work with optically active cobalt–polyamine complexes.

In work with the optically active *cis*-dichlorobis(ethylenediamine)cobalt(III) cation, it was shown that inversion could be caused under certain conditions by displacing the chloride ions with either carbonate or ammine.[1] As was pointed out, the amount of inversion during carbonate substitution was shown to be dependent on several variables. These were concentration of the complex, concentration of the silver ion added, concentration of the carbonate ion present, ratio of hydroxide ion concentration to complex ion concentration, and the reaction sequence. Further, with ammine substitution in liquid ammonia, inversion was noted to be temperature dependent.[2,3] No studies have been reported in which the substituting ligand is an amino acid or an optically active amino acid.

Bailar and McReynolds[4] studied substitutional inversion with the D-*cis*-dichlorobis(*l*-propylenediamine)cobalt(III) ion. However, it is impossible to conclude from their work to what extent the optical activity of

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[3] R. D. Archer and J. C. Bailar, Jr., *ibid.*, **83**, 812 (1961).

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