Table I. Semiempirical SCF MO 1,3 Perturbation Energies ($\Delta E_{1,3}$)

Method	Geometry	$\Delta E_{1,3}$, kcal/mol
CNDO/I	CNDO/II optimum (puckered)	20.4
CNDO/II	CNDO/II optimum (puckered)	29.7
CNDO/I	CNDO/II optimum planar	24.5
CNDO/II	CNDO/II optimum planar	33.5
MINDO/3	MINDO/3 optimum (planar)	32.4

lished report, MINDO/3 fails to ascertain the absolute cyclobutane minimum as puckered.[4] However, CNDO/2 does (at a pucker angle of 20°) when methylene rocking is allowed.[5] Zeroing the appropriate 1,3 matrix elements and reoptimizing (still using CNDO/2) generates the planar form. The greater stability of the puckered form is directly linked to the 1,3 interaction. In a similar fashion, the methylene rocking angle (3° at the CNDO/2 minimum) vanishes when the 1,3 interactions are nullified.

The consequences of 1,3 interactons are even more prominently displayed in the cyclobutyl cation.[6] The MINDO/3 optimum geometry is highly puckered (46.4°), but the pucker completely disappears upon reoptimization sans the 1,3 interaction. At the same time the energy decreases by 27.3 kcal ($\Delta E_{1,3}$ = 27.3 kcal, 5 kcal less than in cyclobutane). The special stability of this cation is thus accounted for in large part by a decrease in 1,3 destabilization. Further analysis shows that the 1,3 interaction is actually bonding, whereas the 2,4 interaction is highly antibonding. These concepts would seem to provide a sounder theoretical basis for discussing such exceptional ions as cyclobutyl and norbornyl than the familiar "steric" and "nonclassical" effects. Another interesting facet of the cyclobutyl cation geometry is the extensive departure from trigonality at C(1), the cationic center. The hydrogen attached to this carbon is bent 36.5° out of the trigonal plane, toward C(3) (i.e., occupying a semiaxial position). Noteworthily, this is opposite to the preferred direction of motion for very close C(1)-C(3) approach, that is, in a bicyclobutane geometry. Optimization sans 1,3 (and 2,4) interactions leaves C(1) precisely trigonal (planar ring). By engendering pyramidal cationic centers 1,3 effects are obviously capable of exerting potent stereochemical effects, such as high exo/endo rate ratios and retentive stereochemistry, on solvolytic reactions. Incidentally, a minor departure from trigonality has even been calculated for the *n*-propyl cation.[7] This, too, can be shown to result primarily from the 1,3 carbon/carbon interaction.

A complex orbital topology effect engenders the 1,3 antibonding overlaps, which are the basis for the general phenomenon of 1,3 carbon/carbon destabilization. More specifically, it is the coupling between these interactions and the numerous long range (generically 1,3) carbon/hydrogen interactions involving C(1,3) and the hydrogens on C(2,4) which account for the observed sign of $\Delta E_{1,3}$. In effect, the C(1)-$H_{C(2,4)}$-C(3) bishomoallylic system is perturbed toward a less stable cyclopropenylic system by the C(1)-C(3) interaction. Orbital occupancies equivalent to a cyclopropenide ion then account for the destabilizing nature of the interaction. This also explains why the 1,3 interactions involving the formally vacant atomic orbital in the cyclobutyl cation are stabilizing.

The observed conformational effects are also qualitatively explicable. In general, the stronger C(1)-C(3) interactions involve σ overlap (i.e., overlap along the C(1)-C(3) axis). Additionally, in the cation the only significant stabilizing interactions involve the vacant orbital. In the planar cation, this stabilizing interaction is purely of the π type and is therefore rather weak. Puckering affords this interaction a large σ component, and pyramidalization further increases this component by orienting the vacant (hybrid) orbital more directly toward C(3). In cyclobutane there are no major stabilizing 1,3 interactions. The task is to minimize the highly destabilizing σ overlaps. The cyclobutane carbon-carbon bonds can be resolved into a transannular component and a peripheral one, orthogonal to the former, in a manner analogous to Walsh cyclopropane. In planar cyclobutane, the transannular overlap is purely σ; in the puckered form the σ component is attenuated.

These calculations and analyses suggest that cognizance of 1,3 carbon/carbon interactions is obligatory in the cyclobutane series.

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The Photoelectron Spectrum of Benzvalene

Sir:

We have measured the He I photoelectron spectrum of benzvalene, $(CH)_6$ (tricyclo[3.1.0.0^{2,6}]hex-3-ene), one of the valence isomers of benzene. Other known isomers fulvene and dimethylene cyclobutene and the valence isomer Dewar benzene have previously been investigated by Heilbronner and co-workers.[1,2]

Benzvalene was synthesized by the method described by Katz, Wang, and Acton,[3] and after purification by gas chromatography was stored under liquid nitrogen. To minimize known decomposition to fulvene on metallic surfaces, an all-glass inlet system was used, and the stainless steel target chamber was coated internally with colloidal graphite. The UV photoelectron spectrometer has been described elsewhere.[4] The benzvalene maintained at −48 °C was admitted to the target chamber through a Teflon needle valve.

The major component of the initial spectral runs was the fulvene impurity readily identifiable through its known spectrum. However, the amount of fulvene contaminant in the spectrum slowly decreased with time as the vapor pressure of fulvene is greater than that of benzvalene and, after several minutes, the spectrum was that of pure benzvalene.

The spectrum given in Figure 1 shows broad unstructured bands, similar to the case of Dewar benzene, and is in contrast to the spectra of benzene and its other isomers. Some indication of vibrational structure, particularly a spacing of about 1000 cm^{-1} on the second band, can be discerned. The main feature of the spectrum is the well-spaced first, second, and third bands followed by strongly overlapped higher bands. The assignment of the spectrum is assisted by reference to calculated molecular orbital eigenvalues.

The ab initio results of Newton et al.,[5] and SPINDO ionization potentials based on the original SPINDO parameters[6] using the microwave geometry of benzvalene,[7] are compared in Table I with the observed vertical ionization potentials. It

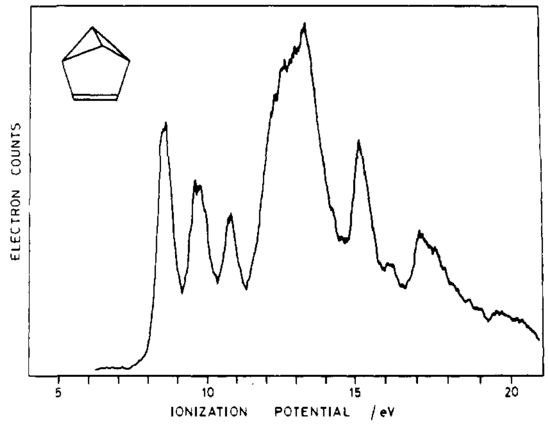


Figure 1. He I photoelectron spectrum of benzvalene.

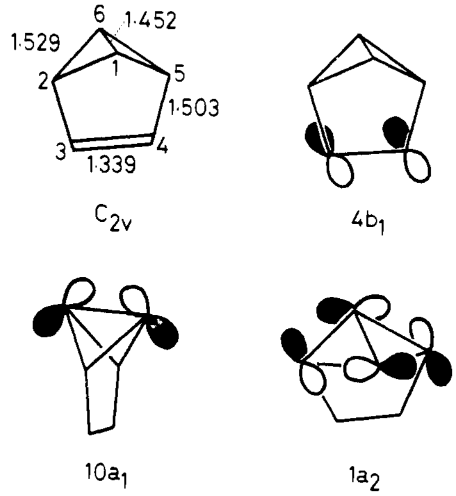


Figure 2. Benzvalene geometry and uppermost occupied molecular orbitals from SPINDO calculation.

Table I. Assignment of Experimental and Calculated Vertical Ionization Potentials for Benzvalene (in eV)

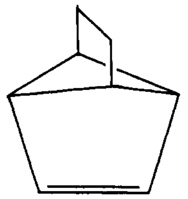
MO	Exptl[a]	Ab initio[b] (-0.9ϵ)	SPINDO[c] ($-\epsilon$)
$4b_1$	8.54	7.8	9.59
$10a_1$	9.60	9.2	10.16
$1a_2$	10.69	10.3	10.57
$6b_2$	12.3	11.9	12.30
$3b_1$	12.7	12.6	12.11
$5b_2$	13.0	12.8	12.48
$9a_1$	13.2	12.9	13.31
$8a_1$	15.1	15.4	14.80

[a] Accuracies vary between ±0.04 and ±0.1 eV. [b] Reference 5. [c] This work.

is noteworthy that the first ionization potential is intermediate in value to those predicted by the ab initio and SPINDO calculations. Otherwise the pattern of photoelectron bands correlates well with both sets of calculated results, which agree except for the order of $3b_1$ and $6b_2$.

The composition of the molecular orbitals associated with the first three bands, as indicated by the SPINDO calculation, are illustrated in Figure 2 together with the benzvalene geometry. The first band is, as expected, related to the π-type $4b_1$ MO of the C_3–C_4 double bond. However, the observation that the band is broad and unstructured indicates that the MO is composed of reasonable contributions from other atoms. The second level is associated with the short bridging C_1–C_6 bond, and relates to an approximate σ-type MO of a_1 symmetry. The third band is involved with the four-center MO of a_2 symmetry.

The low first vertical IP of benzvalene leads us to suspect that the unusual electronic absorption spectrum of benzvalene (λ_{max} 217 nm)[8] is interpretable in terms of a valence shell transition (either $\pi^* \leftarrow \pi$ (b_1) or $\pi^* \leftarrow \sigma$ (a_1)) upon which is superimposed the first member of a low lying Rydberg series (ns $\leftarrow \pi$ or ns $\leftarrow \sigma$). To support this argument we note that the quantum defect of 0.89 is strikingly similar to that observed for tricyclo[3.3.0.0^{2,6}]oct-3-ene of 0.90, where the Rydberg nature of the absorption spectrum (λ_{max} 218 nm) is well confirmed.[9,10]



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New Applications of the Mannich Reaction. Use of Dimethyl(methylene)ammonium Trifluoroacetate for Regiospecific Carbanion Quenching. A New Route to α-Methylene-γ-butyrolactone

Sir:

A new approach to the Mannich reaction has been discovered which permits regiospecific alkylation and convenient derivatization of ketones, esters, and carboxylic acids. This approach employs dimethyl(methylene)ammonium trifluoroacetate, **1**, one of several related Mannich reagents which have become available in the past several years.[1] Our Mannich approach essentially involves trapping pregenerated "carbanions". Because **1** may be utilized in aprotic solvents, this scheme permits an uncoupling of Mannich reactivity from the usual requirement of acidity in a protic solvent. The approach is entirely analogous to carbanion trapping with formaldehyde, a method introduced by Grieco[2] some years ago and more recently applied by Stork[3] to regiospecifically generated anions. Potential advantages of the Mannich approach are less dialkylation, polymerization, and greater product stability.