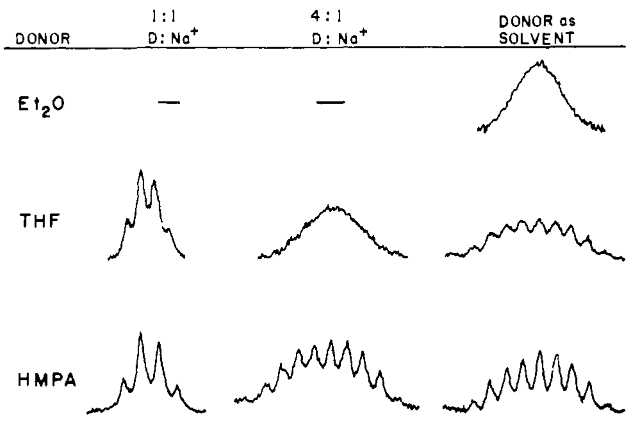

Figure 1. Methylene group resonance patterns in $AlEt_4^-$ for different ratios of donor/Na^+.

Table I. Donor/Na^+ Ratio to Give Solvent Separated Ion Pairs

Donor	D/Na^+ to give $[M^+//X^-]^0$	DN
Ethylenediamine (en)	2:1	
Dimethoxyethane (DME)	3:1-4:1	
Hexamethylphosphoramide (HMPA)	4:1	38.8
Dimethylformamide (DMF)	4:1-5:1 (probably 4:1)	30.9
Dimethyl sulfoxide (Me_2SO)	4:1-5:1	29.8
Pyridine (py)	>18:1	33.1
Tetrahydrofuran (THF)	>18:1	20.0
Diethyl ether (Et_2O)		19.2

HMPA. This has been attributed to an equilibrium between contact and solvent separated ion pairs,[9] but the distinctiveness of the nine-line pattern indicates a predominance of solvent separated ion pairs. On the other hand, when Et_2O is used as the solvent, the methylene resonance is indicative of a preponderance of contact ion pairs, thereby emphasizing the poor donor ability of Et_2O. Thus we see three cases; HMPA is a strong donor giving solvent separated ion pairs at a 4:1 ratio of D/Na^+; THF is an intermediate donor giving solvent separated ion pairs at high D/Na^+ ratios; and Et_2O is a sufficiently poor donor that it does not form solvent separated ion pairs with $NaAlEt_4$.

Analagous studies were made with a number of other donors, and the D/Na^+ ratios necessary to convert contact ion pairs to solvent separated ion pairs are given in Table I.

The observations for pyridine are particularly interesting. The Gutmann donor number for pyridine is 33.1, a very high value, and the correlation by Popov et al. of the ^{23}Na NMR chemical shifts with donor numbers substantiates this value.[11] More recently data has been obtained that brings the donicity of pyridine toward the Na^+ ion into question.[12] Although the results were logically rationalized in terms of solvent-solvent interactions, the observations reported here indicate that pyridine is, in fact, a rather poor donor toward the Na^+ ion. Based on the results of this study, a donicity toward the Na^+ ion similar in magnitude to that of THF would seem to be more reasonable. It is also interesting to note that DME is not as strong a donor as might be expected.

It is apparent from the above that for strong donors, a D/Na^+ ratio of 2:1 for bidentates and 4:1 for monodentates is sufficient to convert a contact ion pair to a solvent separated ion pair. But this is not to be construed to mean that the solvation number of the Na^+ ion is four. In previous studies, a solvation number of four has been proposed for the Na^+ ion,[13] but using Me_2SO as the donor, Wuepper and Popov reported a value of six.[14] Recent studies in this laboratory give support to the Wuepper and Popov value.[15]

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Symptoms of 1,3 Carbon–Carbon Interactions in Cyclobutane and the Cyclobutyl Cation

Sir:

The 1,3 carbon/carbon covalent interaction across a four-membered ring has recently been shown to exert tremendous effects on spin density distributions in cyclobutenoid ion radicals[1] and in cyclobutyl radicals.[2] More than 20 years ago, Dunitz and Shomaker[3] proposed that such interactions are repulsive in cyclobutane and account for a large fraction of its strain energy. This attractive theory seems not to have gained widespread acceptance, though without the postulated effect that near equality of cyclobutane's strain (26.4 kcal) to that of cyclopropane (27.6) appears awkward to rationalize. It should be emphasized that 1,3 strain is absent in cyclopropane, by defintion, and is therefore at a maximum in cyclobutane. The purpose of the present communication is to more convincingly document the role of 1,3 carbon/carbon interactions in cyclobutane strain and, indeed, in a variety of properties of cyclobutane and the cyclobutyl cation.

Semiempirical SCF MO calculations (CNDO/I, CNDO/II, and MINDO/3) were used to estimate the contribution of 1,3 carbon/carbon interactions to the strain energy of cyclobutane. The 1,3 perturbation energy ($\Delta E_{1,3}$) was calculated (Table I) as the difference between the energy obtained in a normal calculation and that obtained in a corresponding calculation in which the Fock matrix elements representing the 1,3 interactions were zeroed. The geometry was held static in the CNDO cases, but is individually optimized in the MINDO/3 calculations. The perturbation energy is seen to range from 20 to 33 kcal (destabilizing), compatible with the suggestion of a major contribution of the effect to the cyclobutane strain.

Explanations of the puckered conformational minimum of cyclobutane emphasize torsional effects, but the results in Table I implicate differential 1,3 interaction energies as a major contributor to this property as well ($\Delta\Delta E_{1,3}$ = $\Delta E_{1,3}$(planar) − $\Delta E_{1,3}$(puckered) = 4 kcal). This conclusion can be tested still more systematically. Contrary to the pub-

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