dependence frequently used in the self-consistent semiempirical methods.

(16) V. Bonacic-Koutecky, *J. Am. Chem. Soc.*, in press.
(17) Compare J. Michl, *Fortschr. Chem. Forsch.*, **46**, 1 (1974).
(18) V. Bonačić-Koutecký, P. Bruckmann, P. Hiberty, J. Koutecký, C. Leforestier, and L. Salem, *Angew. Chem., Int. Ed. Engl.*, **14**, 575 (1975).
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(20) Minima are fairly shallow. For example, the terminally twisted triplet with C–C bond lengths 1.4 Å in the allyl moiety is placed at 1 kcal/mol relative

to the terminally twisted triplet with asymmetrical allylic bond lengths as given in Figure 3.

(21) (a) J. Saltiel, L. Metts, and M. Wrighton, *J. Am. Chem. Soc.*, **91**, 5684 (1969); (b) J. Saltiel, L. Metts, A. Sykes, and M. Wrighton, *ibid.*, **93**, 5302 (1971); (c) J. Saltiel, A. D. Rousseau, and A. Sykes, *ibid.*, **94**, 5903 (1972).
(22) R. S. H. Liu and Y. Butt, *J. Am. Chem. Soc.*, **93**, 1532 (1971).
(23) A. Padwa, L. Brodsky, and S. Clough, *J. Am. Chem. Soc.*, **94**, 6767 (1972).
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1,3 (Nonbonded) Carbon/Carbon Interactions. The Common Cause of Ring Strain, Puckering, and Inward Methylene Rocking in Cyclobutane and of Vertical Nonclassical Stabilization, Pyramidalization, Puckering, and Outward Methylene Rocking in the Cyclobutyl Cation

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Abstract: An analysis of the extensive effects of 1,3 (nonbonded) carbon/carbon interactions in the cyclobutane system is presented. The analysis is based upon MINDO/3 and CNDO/1 and -/2 semiempirical SCF MO calculations in which the specific interactions of interest are zeroed in the Fock matrix. Classical estimates of Baeyer strain (valence strain based upon attenuated overlap) in cyclobutane are found to be in the range 7–11 kcal (as an upper limit), i.e., too small to account for the large (26.4 kcal) experimental cyclobutane strain. On the other hand, the SCF MO calculations yield estimates of 1,3 carbon/carbon repulsions (also termed Dunitz–Shomaker strain) in the range 20–33 kcal, thus suggesting this as the (dominant) companion effect of Baeyer strain in comprising the total strain of cyclobutane. Detailed examination of these 1,3 carbon/carbon repulsions confirm that they should carry over to heats of combustion measurements. The small incremental strain in cyclobutene relative to cyclobutane (2.5 kcal) is also in better accord with the low level of Baeyer strain postulated here, as is the planarity of the cyclobutyl radical. The strain of bicyclo[1.1.0]butane, previously considered anomalously high, is exceptionally well clarified by the concept of Dunitz–Shomaker strain. The variation of the latter type of strain with the pucker and methylene rocking angles provides a unified rationale for both of these additional effects as observed in cyclobutane. Even though puckering shortens the 1,3 carbon/carbon distance, the 1,3 carbon/carbon interaction actually becomes less destabilizing (4.0 kcal) concomitantly with this motion. Dunitz–Shomaker strain in the cyclobutyl cation is 5.1 kcal less than in cyclobutane, in accord with the special stability of this cation. The net interaction between the cationic center and its 1,3 related carbon is now actually bonding. A quantum mechanical basis for both strain relief and vertical nonclassical interactions thus exists. The extensive pyramidalization at the cationic center, as well as methylene rocking in the opposite sense to that in cyclobutane, is also found to be directly and cogently linked to 1,3 carbon/carbon interactions.

In conventional molecular formulas, canonical bonds are used to represent the major interatomic interactions. Generically, these may be designated 1,2 interactions insofar as this implies interactions between directly "bonded" atoms. The interactions between nonbonded atoms are then 1,3 or 1,4 or the like. It can be shown[1] that, of all the nonbonded interactions present in a hydrocarbon molecule, the largest is the 1,3 carbon/carbon interaction. The shortest 1,3 carbon/carbon distances, and therefore potentially the most dramatic manifestations of such interactions, are to be found in the cyclobutane series. Recent studies have documented impressive effects on spin density distributions in cyclobutenoid ion radicals engendered by 1,3 carbon/carbon interactions.[2,3] Significant, though smaller, effects were observed even in molecules with normal valence angles. Other work has implicated 1,3 carbon/carbon repulsions as a component of ring strain in cyclobutane and norbornane.[4] In view of the uniqueness of the 1,3 carbon/carbon interactions within the set of nonbonded interactions and of the cyclobutane series within the aforementioned subset, it appeared fruitful to look for other manifestations of 1,3 carbon/carbon interactions within this series. As will be seen, the catalog of properties which reflect strong

and coherent links to the 1,3 carbon/carbon interaction includes virtually all of the exceptional properties of the cyclobutane system.

Ring Strain. More than two decades ago Dunitz and Shomaker reasoned that repulsive 1,3 carbon/carbon interactions must be responsible for a large component of the strain energy of cyclobutane.[5,6] This seemingly attractive theory seems not to have gained widespread acceptance, though without its postulated effect, the near equality of cyclobutane's strain (26.4 kcal/mol) to that of cyclopropane (27.6) still might appear awkward to rationalize. The foregoing assertion perhaps requires amplification. By definition, cyclopropane has no 1,3 (nonbonded) carbon/carbon interactions. Its ring strain therefore must, apart from torsional effects, be engendered by what will here be termed Baeyer strain, i.e., weakened 1,2 carbon/carbon bonding resulting from poor overlap (decreased σ character in the carbon/carbon bonds).[7] The total angular distortion from ideal tetrahedrality in cyclopropane is $3(109 - 60) = 3(49) = 147°$. Notwithstanding the virtually equal experimental strain energies, the total Baeyer distortion in cyclobutane is only $4(109 - 88) = 84°$. Moreover, for small distortions, angle strain is normally assumed to vary as at least

the square of the individual distortion angle, i.e., $E = \Sigma_i n_i \cdot k \Delta \theta_i^2$, where k is a Hooke's law constant and n_i is the number of angles having distortion $\Delta \theta_i$ from ideality. Substitution of the net (experimental) cyclopropane strain into the foregoing equation yields a value of k (0.003832 kcal/deg^2) which should reflect Baeyer strain alone.[8] The Baeyer strain in cyclobutane computed using this value of k is in fact only 6.75 kcal/mol. The result of this conventional, classical analysis is interesting in that it suggests that some effect other than Baeyer strain, possibly Dunitz–Shomaker strain (1,3 carbon/carbon repulsion), may contribute heavily to the net strain of cyclobutane. Clearly the use of a Hooke's law potential for such large distortions is at best crude, but the estimated contribution of Baeyer strain is decreased even further when account is taken of the fact that the effective k value most probably increases with the distortion angle. In cyclopropene, for example, where two of the distortion angles are greater than in cyclopropane but Dunitz–Shomaker strain is still absent, the experimental strain (53.1 kcal/mol) is considerably underestimated (36.8 kcal) when the cyclopropane k value is used. Thus, the classical estimate (6.75 kcal) of Baeyer strain in cyclobutane probably represents an upper limit.

Roberts and Caserio[9] have pointed out that the true *ring* strain in cyclopropane is actually substantially greater than the experimental strain, since the carbon–hydrogen bonds are strengthened relative to those of acyclic alkanes by hybridization, there being increased s character incorporated into these exocyclic bonds. Assuming, based upon bond dissociation energies, that the C–H bonds of cyclopropane and cyclobutane are 3.0 and 0.5 kcal stabler than those in alkanes, respectively, these authors corrected the *ring* strain energies of cyclopropane and cyclobutane to 45.6 and 30.4 kcal, respectively. These numbers are, of course, more palatable than the raw strain energies, but still leave much room for a major contribution from Dunitz–Shomaker strain in the case of cyclobutane. Following the procedure outlined earlier, one recalculates k = 0.002 555 for cyclopropane and, extending this to cyclobutane, obtains a Baeyer strain upper limit of 11.16 kcal (to be compared with 30.4 kcal of total ring strain in this case).

Moreover, if cyclobutane's strain were actually wholly or even largely of the Baeyer variety, large differential strain effects would be predicted to accompany its conversion to the cyclobutyl radical and to cyclobutene which are not, in fact, observed. Proceeding on the basis of the stated assumption, one obtains k = 0.01496 for a cyclobutane molecule with 26.4 kcal of Baeyer strain. The trigonal cyclobutyl radical (with one $\Delta \theta_i$ = 120 − 88 = 32°) should then be destabilized with respect to the pyramidal form by 8.72 kcal of Baeyer strain. Even a rather small deviation from trigonality should be detectable in the ESR spectrum of this radical, and none is observed.[10] Considering the rather mild inherent preference of carbon radicals for trigonality, the failure of cyclobutyl to depart even slightly from trigonality is rather difficult to reconcile with a differential Baeyer strain of this magnitude. In contrast, the k value (0.003832) based on cyclopropane as representing pure Baeyer strain (27.6 kcal) predicts a differential Baeyer strain of only 2.230 kcal. A quantity of this magnitude could easily be imagined to be dominated by the inherent trigonal preference and by torsional effects. In contrast to the cyclobutyl radical, the cyclopropyl radical is distinctly pyramidal. The differential Baeyer strain corresponding to the smaller k value is 4.59 kcal. In view of the larger than predicted strain of cyclopropene, the actual value is probably considerably higher. Similarly, the differential experimental strain in cyclobutene is only 2.5 kcal (heats of hydrogenation).[11] Employing the smaller k value, the differential Baeyer strain is 2.8 kcal. Using the larger k value, the result is no less than 17.44 kcal. Clearly, no plausible reckoning of torsional effects could reconcile the small measured differential net strain with a Baeyer strain of

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

Method	Geometry	$\Delta E_{1,3}$, kcal/mol
CNDO/1	CNDO/2 optimum (puckered)	20.4
CNDO/2	CNDO/2 optimum (puckered)	29.7
CNDO/1	CNDO/2 optimum planar	24.5
CNDO/2	CNDO/2 optimum planar	33.5
MINDO/3	MINDO/3 optimum (planar)	32.4

this latter magnitude. The low level of Baeyer strain implicit in the differential net strains of cyclobutyl radical and of cyclobutene thus appears compatible with the low level of Baeyer strain estimated for cyclobutane using cyclopropane as a model for pure Baeyer strain, but not with the much higher level of Baeyer strain required were this the only source of strain in cyclobutane.

The Magnitude of 1,3 Carbon/Carbon Interactions. The preceding classical analysis, though too crude to be decisive, indicates that Baeyer strain in cyclobutane is much smaller than either the experimental strain or the ring strain of this molecule, and that some other effect must be contributing preponderantly to these strains. Quantum mechanical estimates of the magnitude of the 1,3 carbon/carbon repulsions (Dunitz–Shomaker strain) in cyclobutane have been obtained and are in just the right range to validate this effect as a plausible partner of Baeyer strain in composing the ring strain of cyclobutane. These repulsion energies were calculated by several semiempirical SCF MO methods (CNDO/1 and /11 and MINDO/3) as the difference between the energies of a normal calculation and that obtained in a corresponding calculation in which the off-diagonal Fock matrix elements representing the 1,3 carbon/carbon interactions were zeroed. In the MINDO/3 calculation, a newly optimized geometry and minimized energy were obtained by additionally zeroing the appropriate bond order matrix elements. The relevant 1,3 carbon/carbon interaction energies ($\Delta E_{1,3}$) are recorded in Table I. The range of from +20 to 33 kcal (the positive sign corresponding to destabilization) is closely comparable with the discrepancy between the classically estimated range for Baeyer strain (7–11 kcal) and the estimated ring strain (30 kcal). It is worth recalling, in connection with these estimates, that all three of the MO methods used tend to overestimate the stability of cyclobutane (underestimate its net strain). It therefore appears somewhat unlikely that they grossly overestimate the Dunitz–Shomaker component of the strain. The 1,3 carbon/carbon repulsion energy in propane, the simplest hydrocarbon molecule possessing such an interaction, was also investigated via CNDO/II and MINDO/3, for comparison with cyclobutane. The much smaller repulsion energy values of 7.62 and 7.77 kcal/mol, respectively, are obtained.

Though plausible in comparison with the cyclobutane repulsion energies (recall that cyclobutane has two such 1,3 carbon/carbon repulsions), a potential query arises concerning why this repulsion is not reflected in the heat of combustion of propane, which, of course, is strainless according to this criterion. To rationalize this, one must analyze the heat of combustion approach to strains in detail, including not just the C–C and C–H canonical bonds, but all 1,3 nonbonded repulsions. The details of this analysis are perhaps not of very general interest, but it is readily seen that, although propane has a sizable 1,3 carbon/carbon repulsion not present in ethane, it has two fewer 1,3 carbon/hydrogen repulsions than the two ethane molecules with which it is being compared in order to model the energies of the two carbon/carbon bonds of propane. Evaluated according to the procedure described above for obtaining 1,3 carbon/carbon repulsion energies, each of these

1,3 carbon/hydrogen repulsions amounts to approximately 3 kcal, thus nullifying all but about 1 kcal of the 1,3 carbon/carbon repulsion effect in propane. Although corrections of this order of magnitude would affect cyclobutane far less seriously, it is nevertheless highly appropriate to inquire to what extent the 1,3 carbon/carbon repulsions calculated for cyclobutane are ultimately reflected in its observed net strain. An analysis similar to the one described above for propane has been performed for cyclobutane, and the relevant correction is, in fact, less than 1 kcal. Both analyses have been carried further, to the level of inclusion of all 1,4 interactions, and no further substantial corrections are found.

From all of the foregoing, it appears likely that Dunitz–Shomaker strain is, in fact, a major contributor to cyclobutane's strain, concurrently with Baeyer strain, and that the former effect substantially exceeds the latter.

The small incremental experimental strain of cyclobutene relative to cyclobutane (2.5 kcal) is nicely consistent with the new formulation of cyclobutane ring strain. The 1,3 carbon/carbon repulsions in cyclobutene are found to be just 2.8 (CNDO/2) or 2.9 kcal (MINDO/3) greater than in cyclobutane. Adding this to the previously estimated incremental Baeyer strain (2.8 kcal), the estimated total incremental strain is 5.6 kcal. Although this does exceed the experimental value, the disparity is small enough to be masked by torsional effects. The essential point is that both Dunitz–Shomaker and Baeyer strains are incrementally small in cyclobutene. It is highly likely that this small increase in Dunitz–Shomaker strain is a consequence of the decrease 1,3 carbon/carbon distance in cyclobutene. Singlet, rectangular cyclobutadiene, for example, is found to have another 2.6 kcal increment of 1,3 carbon/carbon repulsions vis-à-vis cyclobutene. In the (planar, sp^2) cyclobutyl radical this incremental strain is negligibly small (0.2 kcal). In contrast, oxetane is less strained by 2.4 kcal than cyclobutane, a logical consequence of the smaller oxygen orbitals which give rise to diminished 1,3 carbon/carbon overlap and repulsion. Apparently, strain resulting from 1,3 carbon/carbon repulsion is not subject to gross fluctuations within the cyclobutane series.

The cyclobutyl cation is a case of special interest. The estimated 1,3 carbon/carbon destabilization (MINDO/3) is 27.3 kcal, i.e., 5.1 kcal less than in cyclobutane. Diminished Dunitz–Shomaker strain is thus able to account for the unusual reactivity of cyclobutyl derivatives in their cation-forming reactions. Importantly, this satisfying rationalization applies to the computed cyclobutyl cation optimum structure which, as will be discussed more extensively below, is basically classical. Proceeding further with the analysis, zeroing the 1,3 and, separately, the 2,4 carbon/carbon interactions, it emerges that the latter is still antibonding as in cyclobutene, but the former is distinctly bonding. The phenomenon of 1,3 carbon/carbon interactions therefore provides an appealing and basic reconciliation between the ostensibly contending concepts of steric and nonclassical effects as applied particularly to solvolytic reactions of such systems as cyclobutyl and 2-norbornyl. Heterolysis in such systems indeed appears to relieve Dunitz–Shomaker strain (a steric effect) and to produce a cation which is stabilized by a vertical nonclassical bonding interaction. Steric repulsions, in the present sense, and vertical nonclassical interactions are thus merely opposite poles of the same (1,3 carbon/carbon) interaction type. In this connection, two important recent precedents should be mentioned. Schleyer[4] has recognized the existence of 1,3 carbon/carbon nonbonded repulsions in cyclobutane and norbornane, finding that these two molecules cannot be satisfactorily treated by molecular mechanics without explicit inclusion of a term representing such interactions. Traylor[12] has discussed the unusual stabilization of the 2-norbornyl cation in terms of "vertical nonclassical stabilization", meaning stabilization through inter-

actions of C_6/C_2^+ (i.e., 1,3 carbon/carbon interactions) without rearrangement to the bridged, nonclassical structure. Thus, Traylor has already pointed out that special stabilization can be accounted for without invoking extensive (or indeed, any) bridging. The enlightenment provided by these ideas appears sufficient to warrant additional comments at a later juncture in this paper.

Conformation, Hybridization, and Rocking. The MINDO/3 optimum geometry for the cyclobutyl cation (**1**) has a pucker


1
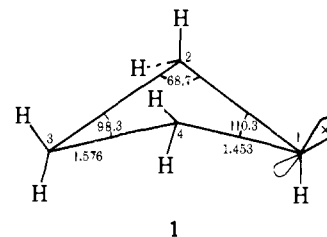
angle of 46.4. Upon reoptimization sans 1,3 carbon/carbon interactions the latter feature completely disappears, concomitantly with the 27.3 kcal decrease in energy, thereby demonstrating conformational control by these interactions. A second interesting facet of the optimized cyclobutyl cation structure is the marked departure from trigonality at C_1, the cationic center. The hydrogen attached to this latter carbon is bent fully 36.5° out of the C_2–C_1–C_4 plane and toward C_3, so that it occupies a quasi-axial position. For comparison, an ideally tetrahedral center would have a 60° bend. It is significant that this is opposite to the preferred direction of movement (**2**) of this hydrogen for very close C_1–C_3 approaches, as


2   **3**
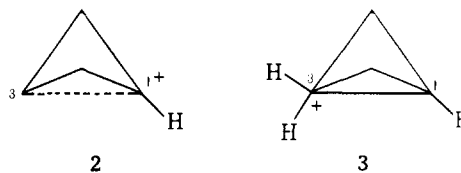
would attend bridging toward a nonclassical bicyclobutane geometry (**3**).

The re-optimization leaves C_1 precisely trigonal. This is, in fact, a rather general phenomenon which appears not to have received attention commensurate to its significance. By engendering pyramidal cationic centers, 1,3 carbon/carbon interactions are obviously capable of exerting important stereochemical influences. In particular, the retentive stereochemistry characteristic of so-called nonclassical systems and the high exo/endo solvolysis rate ratios observed in the 2-norbornyl system are susceptible to rationalization on the basis of this effect (see **4, 5, 6**). Schleyer has found, in an ab initio


4

5

6
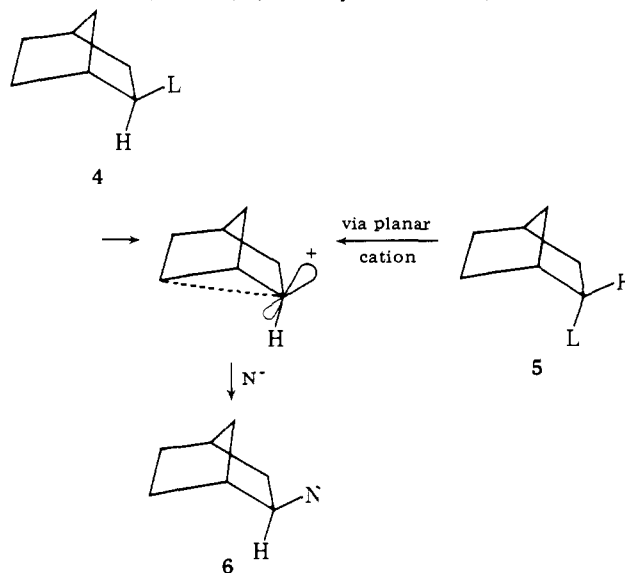
calculation, that even the *n*-propyl cation, the smallest carbonium ion having a 1,3 carbon/carbon interaction, has an appreciable (5.4°) departure from trigonality, although the basis for the effect was not analyzed in detail.[13] MINDO/3 reproduces this nontrigonality, and the standard analysis of all 1,3 and other long-range interactions in the *n*-propyl cation reveals that it is the 1,3 carbon/carbon interactions, again, which are primarily responsible for the effect. Interestingly, the sense of the deviation from trigonality is the same in the case of the cyclobutyl and *n*-propyl carbonium ions, the hydrogen(s) in question (attached to C_1 in either system) moving toward C_3. The effect appears quite general and is easily explicable in terms of maximization of the binding between the vacant orbital at C_1 and the valence shell orbitals on C_3. Structures **7**, **8**, and **9** illustrate that pyramidalization, and specifically that in the observed sense, yields the maximum σ component to the bond mentioned above. Actually the very same effect can be seen to favor puckering in the cyclobutyl cation and the "axial" methyl conformations in the *n*-propyl


| **7** | **8** | **9** |
| planar cation | observed pyramidality | unfavorable pyramidality |
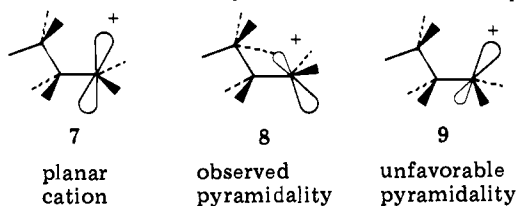
cation, the bonding between the aforementioned centers $(C_1(p_z)-C_3)$ having no σ component at all in the planar cyclobutyl cation or in the *n*-propyl cation conformation in which the methyl group is perpendicular to the p_z orbital orbital at C_1. In addition, puckering in the cyclobutyl case allows closer approach of C_1 and C_3.

Still another effect which is cooperative with ring puckering and pyramidalization, and which is similarly dependent on 1,3 carbon/carbon interaction, is methylene rocking. This is essentially the counterpart at C_3 of pyramidalization at C_1. This rocking angle is defined as the angle between the bisectors of the $H-C_3-H$ and $C_2-C_3-C_4$ angles. The reoptimization sans 1,3 carbon/carbon interactions, of course, causes the rocking angle to vanish also. The connection between these interactions and the rocking angle is wholly analogous to that invoked above for pyramidalization and puckering and is displayed in **10** and **11**, where it can be seen that rocking the C_3 methylenes in the

| **10** | **11** |
| observed rocking | unfavorable rocking |
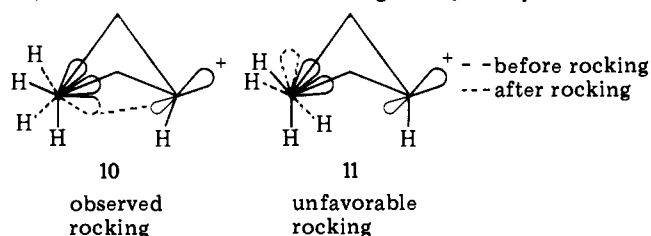
proper sense in effect aims the endocyclic carbon hybrid orbitals more directly toward the vacant orbital at C_1, thereby further increasing the σ component of such bonding.

The relevance of 1,3 carbon/carbon interactions to exo/endo solvolysis rates in the 2-norbornyl and related systems via the pyramidalization factor has been discussed. It seems desirable to call attention to a second effect, also dependent on 1,3 carbon/carbon interactions, which could cooperate with the pyramidalization factor in this connection. An endo leaving group (**12**) interacts simultaneously with C_2 and C_6 in the norbornyl


| **12** | **13** |
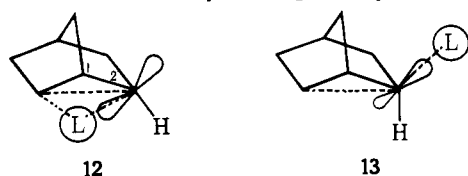
system. The system C_2-L-C_6 therefore constitutes a homocyclopropenide system, which should be less favorable than the allyl anion system present in the case where the leaving group is exo (**13**). This effect is reminiscent of Brown's steric postulate, whereas the pyramidalization effect is more closely related to Winstein's concept of nonclassical interactions.

That each of the four exceptional properties of the cyclobutyl cation (stabilization, puckering, pyramidalization, and rocking) has as its impetus the maximization of C_1-C_3 bonding is, in our view, an impressive exhibition of the importance of these interactions in the cyclobutyl cation system.

As might be expected from the preceding analysis, the conformation of cyclobutane is also powerfully influenced by 1,3 carbon/carbon interactions. Table 1 reveals that the puckered form is less destabilized that the planar one through 1,3 carbon/carbon interactions by 4.1 (CNDO/1) or 3.8 kcal (CNDO/2). Unlike MINDO/3, which erroneously generates a planar cyclobutane minimum, CNDO/2 apparently finds the absolute conformational minimum as puckered (20°),[14] in reasonable agreement with experiment. The methylene rocking angle at the minimum is 3°; zeroing the 1,3 carbon/carbon interactions and reoptimizing results in the disappearance of both the pucker and rock angles, just as in the cyclobutyl cation. This dependence of Dunitz–Shomaker strain on pucker angle can be rationalized in a manner analogous to that discussed for the cyclobutyl cation. In cyclobutane, however, all of the important 1,3 interactions are destabilizing. The 1,3 overlap and hence the destabilization should decrease as the σ character of the 1,3 interaction decreases concomitantly with puckering. An elaboration of this point may be desirable. The carbon orbitals primarily involved in the 1,3 carbon/carbon interactions are the 2s and $2p_x$ orbitals (**14**).


| **14** | **15** |
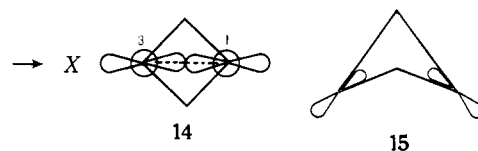
Interaction between the $2p_x$ orbitals on 1,3 related carbons is strongest (and most repulsive) in planar cyclobutane, inasmuch as pure σ overlap is involved. Ring puckering diminishes the σ character of this overlap, reducing the magnitude of the latter as a consequence (**15**). The link between methylene rocking and 1,3 carbon/carbon interactions is explicated similarly. In this case it is especially interesting to note that the sense of the rocking is opposite to that in the cyclobutyl cation, exactly as it should be according to the theory expounded above. Rotation of the endo hydrogens toward each other may be seen (**16**) to confer additional π character on the 1,3 interactions.

16	
	before rocking
	after rocking
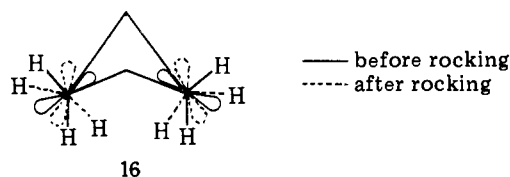
That the 1,3 carbon/carbon repulsions are antibonding in the first place may be regarded as the result of a complex orbital topology effect. In attempting to deduce a simple and explicit explanation of the effect, the magnitude of the 1,3 carbon/carbon interaction was studied in the presence and absence of other, perturbing, interactions. In the case of one interaction type, the 1,3 C/H interaction, the results were dramatic. Specifically, in the absence of these interactions the 1,3 carbon/carbon interactions are actually bonding. Apparently, a coupling of these two effects engenders the 1,3 carbon/carbon repulsions. Although the individual 1,3 C/H interactions, as discussed earlier, are far weaker than the 1,3 carbon/carbon interaction, there are 16 of the former in cy-

clobutane and but two of the latter. The total effects are therefore comparable. The above findings can now be given a qualitative explanation based on familiar principles. The 1,3 interactions of the type $C_1-H_{C_2C_4}-C_3$ form a kind of bishomoallylic system (**17**). The C_1/C_3 interaction perturbs this

17
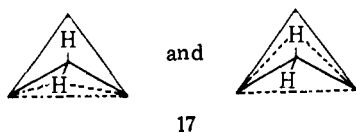
strongly toward a trishomocyclopropenyl system. The orbital occupancy corresponds to that of the anion of the latter system, since an even number of orbitals based on this system are filled. As a result the 1,3 carbon/carbon interaction is strongly destabilizing for the same reasons that the cyclopropenide ion is less stable than the allyl anion.

Cyclobutyl Anion. It was previously noted that MINDO/3, in predicting a preferred planar conformation for cyclobutane, errs in the direction of underestimating the stability of the puckered form relative to the planar one. It was therefore somewhat surprising to find that the cyclobutyl anion is optimized in the puckered form (8.1°). Perhaps equally unexpectedly, the Dunitz-Shomaker strain in the anion (30.97 kcal) is less than for cyclobutane. The cyclobutyl cation and anion are thus qualitatively similar in both of these respects. The anionic carbon (C_1) of the latter is also pyramidal, the attached hydrogen being displaced at 31.4° out of the $C_2-C_1-C_4$ plane toward a quasi-equatorial position. The simple notion that the electron pair is larger than a carbon–hydrogen bond, of course, predicts the hydrogen to prefer an axial position. Once again, 1,3 carbon/carbon interactions supply the missing explanation. An axial lone pair has only π 1,3 carbon/carbon interactions, of course, whereas an equatorial pair interacts with C_3 via a large σ component. This now familiar line of thought also leads to an appealing explanation of the puckering and strain effects referred to above. It is a familiar fact that, in SCF calculations, charge densities tend to alternate from atom to atom. Thus where C_1 is negatively charged, C_2 is positively charged, etc. A less frequently invoked effect is the analogous "alternation" in orbital charges. In the present cyclobutyl anion calculation the lone pair occupies a hybrid orbital which is oriented in the z direction. Accordingly, the p_z and 2s charge densities are found to be 1.5762 and 1.3164, respectively. In order to minimize the charge buildup and hence the electronic repulsions at C_1, the p_x and p_y orbitals are electron deficient, the relevant charge densities being 0.8183 and 0.8517, respectively. The p_x orbital is the one primarily involved in the C_1/C_3 interaction and, being electron deficient, produces effects similar to those found in the cyclobutyl cation, viz., reduced Dunitz-Shomaker strain used an enhanced tendency (relative to cyclobutene) toward puckering.

It may be of interest to comment briefly on the Fock matrix element zeroing technique employed in this work. The approach involves setting to zero the one-electron, two-center integrals (β in the Hückel approach) involving orbitals situated on the selected atoms (1,3) and (a much smaller effect) the exchange integrals involving the same orbitals. Coulomb repulsion integrals are not affected. In effect, the result is a perturbational treatment of very high order. One might reasonably ask, since SCF energies can be partitioned into inter-

actions involving the various integral types in the various bonds, why this simple approach was not adopted. In fact, the latter approach can be highly misleading. In cyclobutane, for example, the 1,3 interaction is so strongly antibonding that the wave function is extensively perturbed so as to minimize this interaction. A direct consequence is the weakening of the canonical C–C bonds. In looking at the partitioned 1,3 carbon/carbon contribution to the energy of cyclobutane by this method, a major component of the destabilization, that which is associated with the weakened C–C bonds, is missed.

Strain Energies in Small-Ring Bicyclo[*n.m*.0]alkanes. It has been noted that strain energies in systems of the aforementioned type are remarkably additive. The strain energy obtained for bicyclo[2.1.0]pentane, e.g., using Franklin group equivalents is 53.6. This should be compared to the sum of the cyclobutane and cyclopropane strains (54.0 kcal). The single known exception, albeit a dramatic one, is bicyclo[1.1.0]butane, which has an experimental strain of 63.9 kcal, in contrast to the additivity prediction of 55.2 kcal. The discrepancy of approximately 9 kcal coincides relatively well with the estimates given herein of a single 1,3 carbon/carbon repulsion in cyclobutane (10–16 kcal). In this view, bicyclobutane should be expected to have the Baeyer strain of two cyclopropane rings and (approximately) one-half the Dunitz-Shomaker strain of cyclobutane.

Conclusions

The conclusions appears inescapable that cognizance of 1,3 carbon/carbon interactions is obligatory in the cyclobutane series. Such interactions qualitatively and quantitatively explain, in a clear and unified way, a host of exceptional properties of the series. Qualitatively similar effects exist in systems with normal valence angles. Increased attention to these effects in all systems therefore seems warranted.

References and Notes

(1) And has been shown, at the semiempirical SCF MO level, in this work.
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(8) To be more precise, the torsional strain should be deducted from the total strain to obtain Baeyer strain. Unfortunately, this can only be done by assuming eclipsed cyclopropane or cyclobutane bonds to have torsional destabilizations equal or similar to that in ethane. This crude approach, it is felt, seriously overestimates the torsional component in cyclopropane and cyclobutane because the 1,4 H/H interactions, upon which torsional destabilization is dependent, are much weaker in these two molecules than in ethane. This follows from the distances in these molecules and has been verified by SCF–MO calculations. In any event, the torsional component is undoubtedly a small component of the total strain in either cyclic molecule, and its neglect should occasion no serious error.
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