

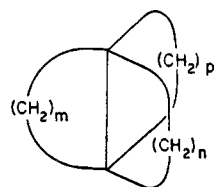
The Electronic Structure and Reactivity of Strained Tricyclic Hydrocarbons

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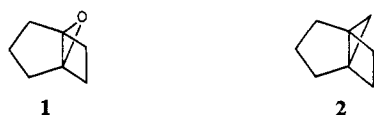
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Abstract: Molecular orbital calculations are presented for the tricyclo[*m.n.p.*0]alkanes with *m,n,p* = 2,2,2, 2,2,1, 2,1,1, 1,1,1, and 3,2,1, and for their interaction with model acids and bases. In the 2,2,2 system the optimum alignment for through-bond coupling of radical lobes creates the conditions for a new kind of isomerism—two stable conformations related by a simple bond stretching. These are the normal tricyclic form **3** and the stabilized diradical **7**. The latter is predicted to be unstable with respect to fragmentation to a dimethylenecyclohexane. The other tricyclic systems are characterized by a single energy minimum. We have studied the reactivity of these strained molecules by both explicit calculations of energy surfaces for the approach of model acids and bases and by perturbation and symmetry arguments. These tricycloalkanes should be susceptible to acid and radical attack at the strained bridgehead bond but relatively inert to the action of base. The general conditions for the stabilization of a trigonal-pyramidal distortion of tetrahedral carbon are given.

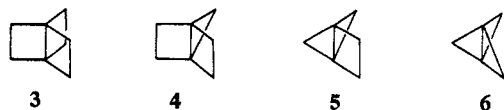
The tricyclo[*m.n.p.*0]alkanes, for small *m*, *n*, and *p*, present the opportunity for realizing an interesting



distortion of a tetracoordinate carbon center, namely the coercion of all four bonds from the bridgehead carbons into one hemisphere. The first such system, **1**, was synthesized by Wiberg and coworkers.^{1a} The synthesis of the parent tricyclo[3.2.1.0^{1,5}]octane (**2**)



and substituted derivatives followed.^{1b,2} Synthetic efforts directed at the still more strained members of this series, **3**, **4**, **5**, and **6**, are no doubt in progress at this time.



Our own theoretical interest in these molecules was originally focused on the fascinating possibilities for through-bond coupling in the symmetrical species **3**. The evolution of this interest into a general exploration of the electronic structure of tricyclo[*m.n.p.*0]alkanes is detailed in this paper.³ It has led us not only to some interesting structural conclusions but to a deeper understanding of the reactivity of strained bonds and the mechanism of fragmentation reactions.

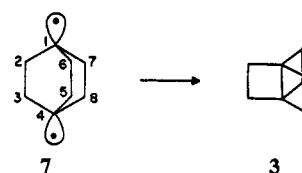
(1) (a) K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, *Tetrahedron Lett.*, 5855 (1968); (b) K. B. Wiberg and G. J. Burgmaier, *ibid.*, 317 (1969).

(2) P. G. Gassman, A. Topp, and J. W. Keller, *ibid.*, 1093 (1969).

(3) *Ab initio* calculations on the tricyclo[1.1.1.0]pentane are reported in the accompanying paper: M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 773 (1972).

Tricyclo[2.2.2.0^{1,4}]octane

Among the more obvious approaches to this tricyclic molecule is the intramolecular recombination of the appropriately generated bicyclic diradical **7**. But this



radical dimerization is less obvious than it seems to be at first glance. It is a symmetry-forbidden reaction! Figure 1 shows an extended Hückel⁴ (EH) calculation of the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, and the total energy of the octane as a function of the C₁-C₄ distance *R*.⁵ We clearly see that HOMO and LUMO cross at *R* = 2.25 Å. This unusual behavior is easily understood from an analysis of through-bond coupling⁶ in **7**.

From the two axial orbitals at C₁ and C₄ one may form two combinations as shown below. One of these is symmetric (S), the other antisymmetric (A) with respect



to the mirror plane perpendicular to the threefold axis. Direct through-space interaction in the highly strained geometry of **3** would be expected to place the symmetric

(4) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers; R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); *ibid.*, **37**, 2872 (1962). The hydrogen 1s exponent was 1.3.

(5) For the octane we used an idealized geometry with C-C 1.54 Å, C-H 1.10 Å, and *D_{3h}* symmetry maintained. The methylene hydrogen positions were consistently varied with *R* so as to keep them, for example at C₂, in the plane bisecting the C₁-C₂-C₃ angle. Deviations from *D_{3h}* symmetry in the related bicyclo[2.2.2]octane are minor, though highly interesting. For a discussion of this problem, see G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967); O. Ermer and J. D. Dunitz, *Helv. Chim. Acta*, **52**, 1861 (1969); A. Yokozeki, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jap.*, **43**, 2017 (1970), and references therein.

(6) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

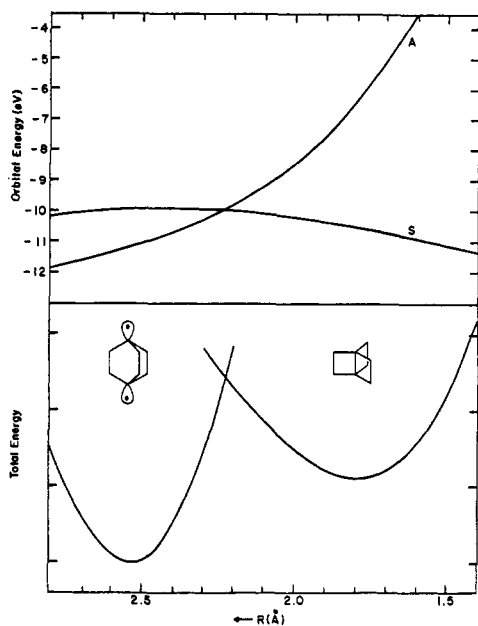


Figure 1. HOMO and LUMO energies (top) and total configuration energies (bottom) as a function of C_1-C_4 distance R in tricyclo[2.2.2]octane. The energy scale interval in the bottom of the figure is 0.5 eV between heavy marks.

combination, the σ level, at lower energy than the anti-symmetric σ^* level. In the extreme geometry of the diradical **7** the separation between centers 1 and 4 is so large that the direct interaction between the axial hybrids is expected to be minimal. However, the geometrical conditions are ideal for through-bond interaction with the σ and σ^* levels of bonds 2-3, 5-6 and 7-8. We have analyzed this interaction in detail elsewhere.⁶⁻⁸ The important symmetry-determined conclusion is that as a consequence of such an interaction the A molecular orbital is at lower energy. Moreover, the geometrical requirements for through-bond coupling are optimally met in the geometry of **7**—witness the remarkable 2.1-eV splitting of the lone-pair combinations in diazabicyclo[2.2.2]octane.⁹

The anticipated level crossing at some value of R is confirmed by the EH calculation shown in Figure 1. That the open diradical minimum is more stable than the closed form may not be a reliable conclusion. Thus CNDO/2 and INDO¹⁰ calculations, while predicting the S-A level crossing at the very same R as EH, make **3** more stable than **7**. Another question that will only be answered by calculation better than ours is the extent to which the double minimum implied by the semiempirical calculations will survive when configuration interaction is introduced.¹¹ The true singlet wave function will be of the form $c_1(S)^2(A)^0 + c_2(S)^0(A)^2$ with

(7) (a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); (b) R. Hoffmann, E. Heilbronner, and R. Gleiter, *ibid.*, **92**, 706 (1970); (c) J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970).

(8) Note especially the closely related case of the tetramethylene diradical: R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(9) P. Bischof, J. A. Hashmal, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969); E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, **92**, 3818 (1970).

(10) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

(11) *Ab initio* calculations on **4**, **7**, and related molecules are in progress. J. Schulman, private communication.

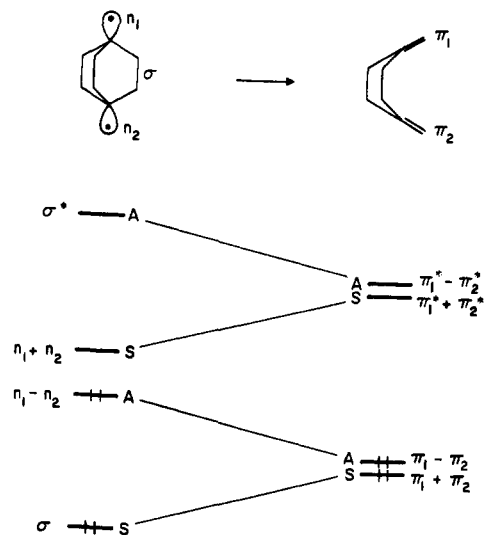
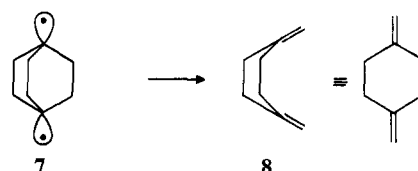


Figure 2. Level correlation diagram for $2s + 2s$ fragmentation of diradical **7**. The mirror plane bisects the breaking σ bond and interchanges n_1 and n_2 .

$c_1 > c_2$ at small R , $c_1 < c_2$ at large R . It is conceivable that the activation barrier between $(S)^2$ and $(A)^2$ configurations will be strongly reduced when electron interaction is introduced in the calculations, but in the subsequent discussion we will assume that a nontrivial barrier separates the two minima.

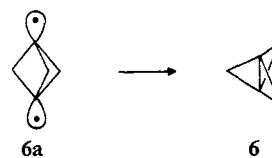
Our enthusiasm at uncovering a novel type of isomerism balancing through-space *vs.* through-bond coupling, $\mathbf{3} \rightleftharpoons \mathbf{7}$, was quickly tempered when we realized that the fragmentation of the diradical **7** to the 1,4-dimethylenecyclohexane (**8**) is a symmetry-allowed



process. This is demonstrated by the correlation diagram of Figure 2. Of course this implies immediately that generation of the diradical **7** is not a good route to **3**. The diradical, if generated, is likely to undergo the thermodynamically favored allowed fragmentation to the cyclohexane.

Other Tricyclo[*m.n.p.*0]alkanes

Our conclusions concerning the level crossing during the diradical dimerization $\mathbf{7} \rightarrow \mathbf{3}$ are strengthened by the computation of the analogous surface for the other tricyclic compounds **2**, **4**, **5**, and **6**. Total energies as well as HOMO and LUMO positions are shown in Figure 3. In the tricyclo[1.1.1.0³]pentane (**6**) the through-bond coupling reinforces the already dominant through-space effect.^{7a} At all reasonable values of R the symmetric level is below the antisymmetric.³ There is only one minimum corresponding to the highly

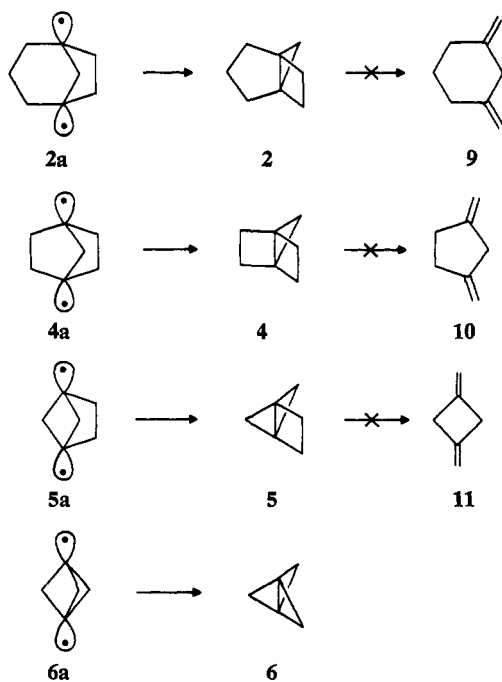


strained **6**. If we imagine the formation of a biradical **6a** in a geometry close to that of the parent bicyclo[1.1.1]pentane ($R = 1.85 \text{ \AA}^{12}$), then such a species should collapse along a path of uniformly decreasing energy to **6**.

The tricyclohexane and tricycloheptane systems **5** and **4** are intermediate between **6** and **3**. Each two-carbon bridge incrementally increases the through-bond coupling capability which stabilizes the A orbital at large R . In **5** the effect shows up only in the slope of the A orbital. In **4** a real level crossing occurs, but at such large R that the minimum (A)² will generate at most a minor inflection in the rapidly rising potential surface. In **2**, the only known compound of the series, there is sufficient geometrical flexibility to assure that through-space coupling dominates at all reasonable R .¹³ The predictions of equilibrium bond lengths in the (S)² minima of **2**, **3**, **4**, and **5** need not be reliable either because sufficient freedom of geometry was not allowed or more likely because of the well-documented unreliability of EH bond lengths.⁴ The central bond length in **2** is known to be 1.54 \AA .¹⁴

The conclusion we have reached is that the "diradicals" **2a**, **4a**, **5a**, and **6a** are but stretched conformations of their collapsed σ -bonded tricyclics **2**, **4**, **5**, and **6** (see Chart I). To **2**, **4**, and **5**, in turn, the $2_s + 2_s$ frag-

Chart I



(12) J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 1614 (1970).

(13) We should remark here on the geometrical assumptions in these studies. For all molecules we assumed that the three bridges go off at dihedral angles of 120° . For **2** we allowed the central carbon of the trimethylene bridge (C_3) to move out of the plane defined by $C_1-C_2-C_4-C_5$. Partial optimization of the angles at C_2 , C_3 , and C_4 , subject to C_s symmetry, was attempted. There are minima for C_3 bent toward the CH_2CH_2 and also toward the CH_2 bridge, the latter being at slightly lower energy, in accord with a preliminary structure determination (ref 14). The situation is similar to that in the related bicyclo[3.1.0]hexane. See M. S. Bergqvist and T. Norin, *Ark. Kemi*, **22**, 137 (1964); K. Tori, *Chem. Pharm. Bull.*, **12**, 1439 (1964); H. E. Smith, J. C. D. Brand, E. H. Massey, and L. J. Durham, *J. Org. Chem.*, **31**, 690 (1966); A. Diefferbacker and W. von Philipsborn, *Helv. Chim. Acta*, **49**, 897 (1966); P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965); S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, **8** (II), 621 (1966).

(14) K. B. Wiberg, private communication.

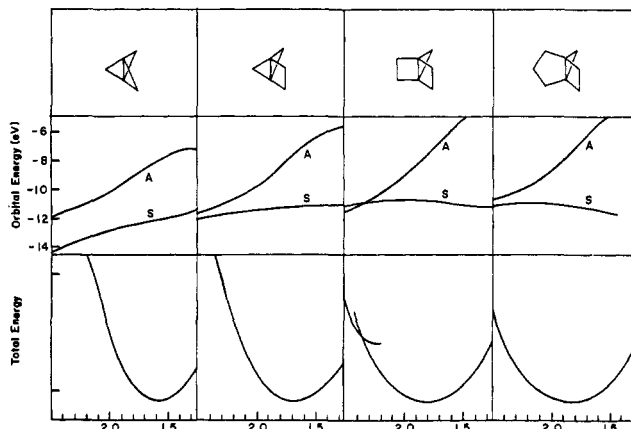
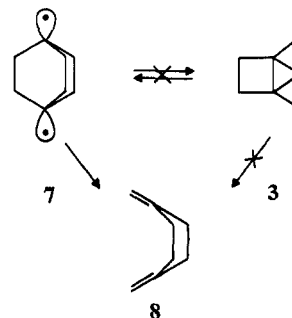


Figure 3. HOMO and LUMO energies (top) and total configuration energy (bottom) as a function of R for various tricycloalkanes. The energy scale interval in the bottom of the figure is 5 eV.

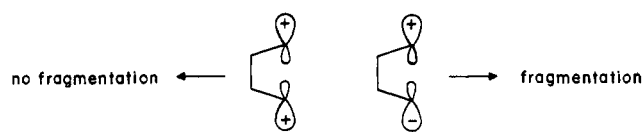
mentation to a dimethylenecycloalkane is a forbidden reaction.¹⁵ This is to be contrasted to the diradical **7**, which is not an unstable conformation of **3** but essentially an isomer of it.



An interesting feature of the predicted allowed or forbidden nature of the $2 + 2$ fragmentations of **2**, **3**, **4**, **5**, and **7** is that these may be viewed as homopolar Grob fragmentations. Grob, in a series of perceptive contributions, has established the conformational requirements for concerted fragmentation,¹⁶ namely an alignment of bonds such as that shown in **12** or **13**.



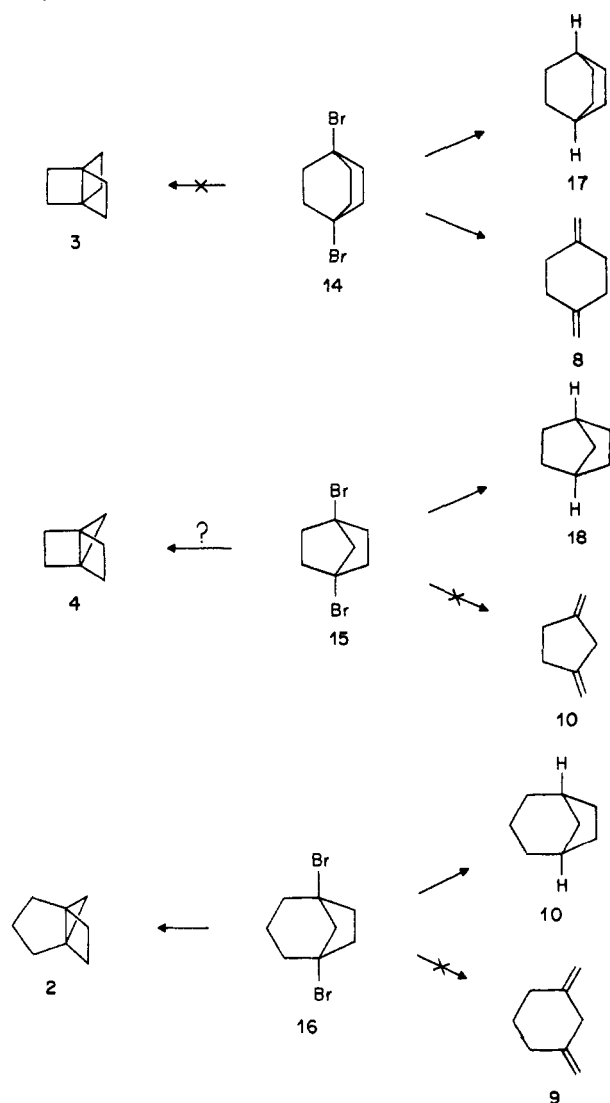
These geometries are recognized as those maximizing through bond coupling of the relevant orbitals. To the conformational prerequisite we must add an electronic one: symmetry-allowed fragmentation will occur only if the occupied orbital is antisymmetric, *i.e.*, when through-bond coupling dominates. While in the tri-



(15) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(16) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955); C. A. Grob and P. W. Schiess, *Angew. Chem.*, **79**, 1 (1967); C. A. Grob, *ibid.*, **81**, 543 (1969).

Chart II

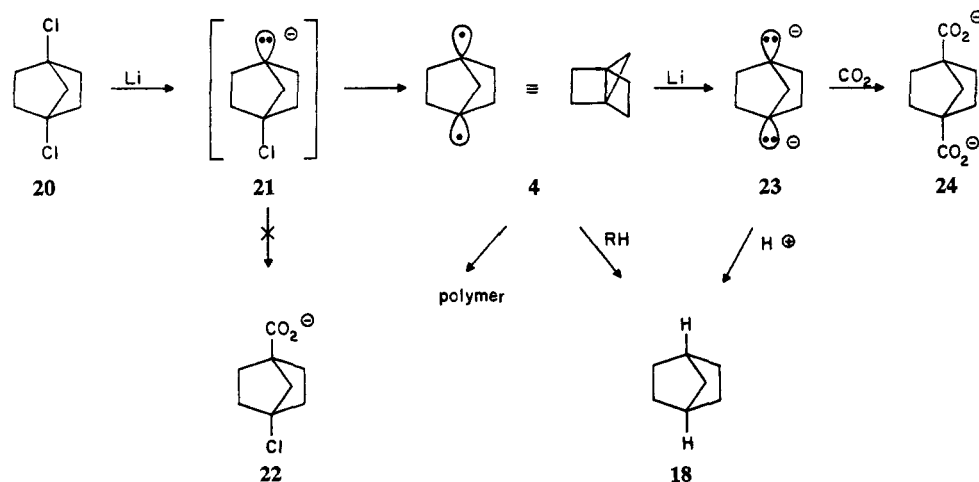


the experimental behavior of the dibromo compounds **14**, **15**, and **16** under debromination by alkali metals (see Chart II).^{14,18} The 1,4-dibromobicyclo[2.2.2]octane (**14**) forms under debromination conditions the 1,4-dimethylenecyclohexane (**8**), as well as some saturated product **17** via hydrogen abstraction from the solvent, but no tricyclooctane (**3**) is detected. On the other hand, the dibromobicyclo[2.2.1]heptane (**15**) forms no fragmentation product **10**, but only the saturated norbornane **18**. Similarly **16** does not undergo fragmentation.^{14,18} The absence of the fragmentation reactions **15** → **10** and **16** → **9** is all the more surprising given the large strain release in these systems. This becomes understandable in view of our analysis—the diradicals formed from **15** or **16** do not have the proper level ordering for allowed fragmentation to **10** or **9**, respectively.¹⁹

The debromination of **15** does not yield the symmetry-allowed collapse product **4**. But there is some evidence that this tricycloheptane is transiently formed. Wilcox and Leung²⁰ found that in the conversion of the dichloro compound **20** to the diacid **24** with Li and CO₂ (see Chart III) (a) the chloro acid **22** was not formed, the intermediate anion **21** obviously having too short a lifetime to react with CO₂, and (b) the diacid is formed in reasonable amounts only if the dichloro compound is added in small amounts to an excess of Li and CO₂. Both results can be explained, as Wilcox²⁰ and Wiberg²¹ have pointed out, by the intermediate formation of the tricycloheptane. The dichloro compound **20** is reduced to the chloroanion **21**, which immediately loses Cl⁻ to form **4**. The tricycloheptane, being very unstable, either, in excess of Li, is further reduced to the dianion **23**, which reacts with CO₂ to the diacid **24**, or, if there is insufficient Li for further reduction, abstracts H from solvent to form norbornane or polymerizes.

The reason why the tricyclooctane (**2**) is easily formed and stable, while the tricycloheptane (**4**) with the same electronic configuration is not found, must be due to the

Chart III



cycloalkanes **2**, **4**, and **5** the geometrical requirement is met, the electronic one is not, since through-space coupling dominates. Fragmentation should not occur. Our conclusions concerning the Grob fragmentation will be the subject of a separate paper.¹⁷

Our theoretical conclusions concerning the electronic structure of these tricyclic compounds are supported by

(17) W.-D. Stohrer, R. Gleiter, and R. Hoffmann, *Helv. Chim. Acta*, in press.

greater strain in the latter. Unlike the tricyclooctane,

(18) P. G. Gassman, Reaction Mechanisms Conference, Santa Cruz, Calif., 1970, and private communication.

(19) So far we have assumed that these reactions take place through the diradicals, rather than by the alternative reaction of intermediate monobrominated monoanions. We will provide elsewhere (ref 17) the demonstration that the conclusions apply to the latter pathway as well.

(20) C. F. Wilcox and C. Leung, *J. Org. Chem.*, **33**, 877 (1968), and private communication.

(21) K. B. Wiberg, E. C. Lupton, Jr., and G. J. Burgmaier, *J. Amer. Chem. Soc.*, **91**, 3372 (1969).

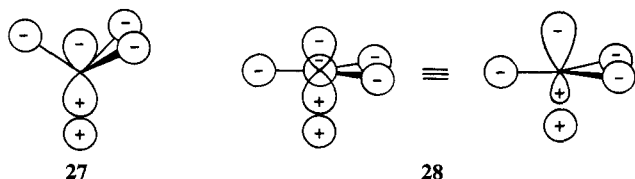
the tricycloheptane cannot in any way readjust internal angles to orient the bridgehead lobes toward each other. As one progresses down the series of compounds from **2** to **6** indeed the observed overlap population in the $(S)^2$ minimum decreases to a value of 0.36 for **6**. Even in the most highly strained compound the gap between HOMO and LUMO is sufficient to ensure a singlet ground state, but the electron density progressively moves out of the region of the bond to the backside of the bridgehead carbons.

Stabilization of Trigonal-Pyramidal Tetracoordinate Carbon

Consider a simple methane, artificially distorted to a C_{3v} geometry with three hydrogens and the carbon in one plane (**25** \rightarrow **26**). The methane valence orbitals

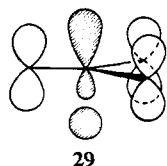


consist of an a_1 and a triply degenerate t_2 . The latter set splits into $e + a_1$ under the C_{3v} distortion, with the a_1 orbital severely destabilized and largely responsible for the energetic cost of the distortion.²² The shape of the a_1 orbital in T_d and distorted C_{3v} geometries is shown below. While the 2s coefficient in **28** is small



(ratio of 2s/2p coefficients is 0.18) the mixing is in just that direction required to produce a hybrid pointing away from the unique C–H bond.

It becomes of interest to describe the conditions for stabilizing the trigonal-pyramid coordination of carbon **26**, just as we have discussed elsewhere the prerequisites for stabilization of planar tetracoordinate carbon.²³ The crucial destabilized orbital, a_1 , **28**, can be depressed in energy by substituting for the three basal hydrogens groups which are good π -electron acceptors, *i.e.* possess low-lying unoccupied molecular orbitals. If oriented as in **29** such orbitals possess the correct symmetry for



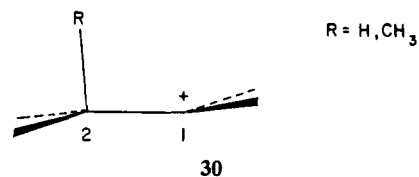
interaction with the high-lying orbital **28**. Thus in R_3CH species we would anticipate decreased energy differences between T_d and C_{3v} geometries for $R = CN$, COR , NO_2 , NO , SiH_3 , etc. The trend has been confirmed by us in an extended Hückel calculation on tricyanomethane. The energy required to change from T_d to C_{3v} ($H-C-CN$ angles 90°) is 0.87 eV, compared to 1.15 eV for the parent CH_4 .

A striking independent confirmation of the soundness of our argument is found in the recently published com-

(22) B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 593 (1971).

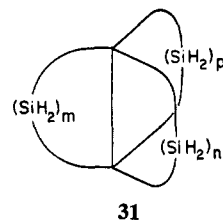
(23) R. Hoffmann, R. Alder, and C. F. Wilcox, *ibid.*, **92**, 4992 (1970).

puted equilibrium structures for ethyl cation²⁴ and primary propyl cation.²⁵ In these systems carbon 2 (see structure **30** below) is substituted by an electron

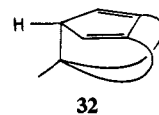


acceptor *par excellence*, the vicinal carbonium ion center at C_1 . The geometrical response of **30** is to reduce the $R-C_2C_1$ angle from tetrahedral and move the hydrogens at C_2 up toward R.²⁶ These readjustments of geometry could be viewed as movements part way toward a symmetrical "nonclassical" carbonium ion structure. Instead we choose to see in these geometrical distortions the formation of a trigonal-pyramidal geometry at C_2 , facilitated by the substituent CH_3^+ .

Unfortunately few of the substituent patterns which we think will stabilize a C_{3v} distortion can be functionally combined with the propellane skeleton. Silyl bridges, as schematically indicated in **31**, could provide



one practical example. A π -electron system could also serve as an acceptor, and a combination with strain driving toward a C_{3v} geometry might be achieved as schematically shown in **32**.



Interaction with Acids and Bases

The chemical reactivity of strained tricyclic systems is our next concern. Two features pointing toward potentially high reactivity with acids and bases are present. First there is an accumulation of electron density in the region of space most exposed to external attack—the backside of the bridgeheads.³ Second, whereas the molecules in question are not diradicals, the strain does make itself felt in creating high-lying occupied and low-lying unoccupied molecular orbitals. This in turn confers upon these molecules good electron donor and acceptor capabilities.

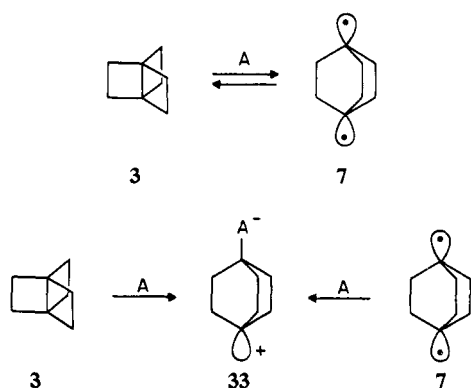
We focus our attention first on the more complicated tricyclo[2.2.2.0]octane (**3**), attacked more or less along the axis of the strained bond by a Lewis acid A (see Chart IV). We explore two questions: (1) does the

(24) J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970); W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971).

(25) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **93**, 1813 (1971).

(26) Another interesting calculated distortion, the weak pyramidality at C_1 , is discussed in ref 24 and 25.

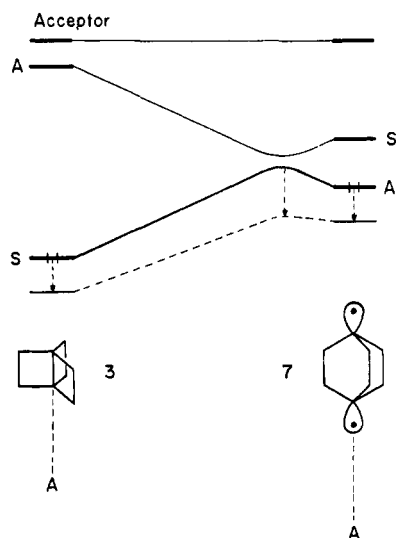
Chart IV



mere presence of the acid reduce the activation barrier for the symmetry-forbidden transformation of $3 \rightarrow 7$, and (2) what can be said about the reaction of the acid with the tricyclo compound 3 relative to its reaction with the diradical 7 , in both cases yielding 33 ?

The problem is most easily treated by studying the perturbation of the correlation diagram for $3 \rightarrow 7$ by the acid. In the diagram shown below (Chart V) we

Chart V



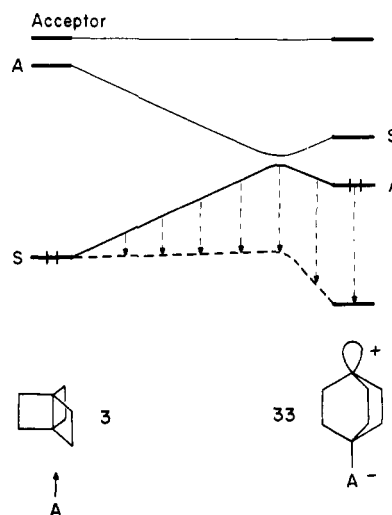
reproduce the correlation diagram for the forbidden $3 \rightarrow 7$ transformation along with the acceptor level of the acid. It is assumed that the acid is at a certain constant distance from C_1 along the entire range of the correlation diagram. The stabilization of the system hinges upon the interaction of the acid (acceptor) with the highest occupied level (S near 3 , A near 7 ²⁷). Since the overlap between the acceptor and the C_1 orbital lobe is approximately constant along the reaction coordinate, the interaction magnitude will be approximately controlled by the energy gap between the highest occupied level of the tricyclooctane and the acceptor orbital of the acid. This energy gap is clearly least, and therefore the interaction maximal, in the region of the transition state. The arrows in Chart V indicate the estimated perturbation. Clearly a lower activa-

(27) Strictly speaking, S and A are no longer proper labels since D_{3h} symmetry is lost in the presence of the acid. Nevertheless, the identity of the orbitals is preserved and they may be identified by their symmetries in absence of the perturbation. Similarly, in Chart V we should indicate the effects of the perturbation on the higher two levels, since all three levels interact in C_{3v} . For reasons of simplicity we show only the chemically significant effect on the lowest level.

tion energy for the transformation $3 \rightleftharpoons 7$ results, *i.e.* acid catalyzes this reaction.

A similar argument may be constructed for analyzing the concerted formation of the open zwitterion 33 by the attack of acid A on the closed tricyclooctane (3). Consider the interaction diagram shown below (Chart VI), in which the acceptor orbital is assumed to ap-

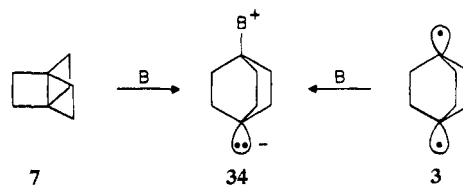
Chart VI



proach closer and closer to C_1 as one moves from left to right in the correlation diagram. Note the contrast to Chart V where the acceptor is assumed to be at the same distance from C_1 throughout the diagram. In the present case we estimate that it is the increasing overlap with the C_1 lobe, the numerator in the perturbation term,⁶ which dominates the interaction. The stabilization is negligible when A is distant from the tricyclooctane, increases in the region of the level crossing, and is maximal when the new C_1 -A bond is fully formed. The activation barrier for the reaction $3 + A \rightarrow 33$ is clearly reduced from that of $3 \rightarrow 7$. This implies that the stability of the tricyclo compound against acid should be less than its thermal stability.

Our qualitative conclusions were checked by a two-dimensional potential surface for the C_{3v} approach of a model Lewis acid, BH_3 , to the system $3 \rightleftharpoons 7$. In this surface, exhibited in Figure 4, the C_1 - C_4 and C_1 -B distances are the independent variables. The right border of the figure, where C_1 - C_4 is varied for C_1 -B ∞ , corresponds to the slice shown previously in Figure 1. Examination of the surface as BH_3 approaches fully confirms our qualitative analysis. Even weak interaction with BH_3 strongly decreases the activation energy, and a stronger interaction removes it entirely. The tricyclo compound and the diradical both fall down to the same minimum, the opened zwitterion 33 .

The approach of a model Lewis base, NH_3 , exhibits the behavior shown in Figure 5. Note the presence now of three distinct minima, the open and closed hydrocarbons 7 and 3 , and the open zwitterionic adduct,



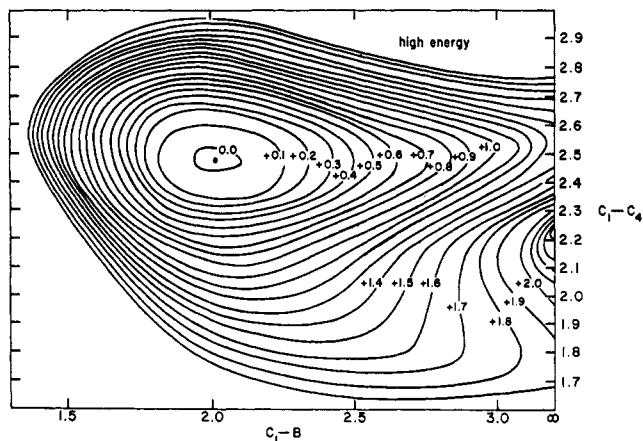
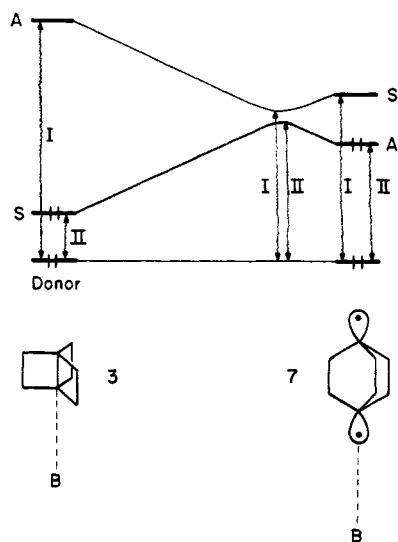


Figure 4. Energy contours in electron volts for the approach of a pyramidal BH_3 to the tricyclo[2.2.2.0]octane system. The energy zero is arbitrarily chosen at the most stable point. The vertical axis is the $\text{C}_1\text{-C}_4$ distance, the horizontal axis the B-C_1 distance.

34. The base does not catalyze the reaction, *i.e.* interaction with NH_3 at no point creates a lower activation energy for the interconversion of **3** and **7**.

The general features of this surface may be explicated from an interaction diagram such as that shown below (Chart VII). Here again the simple forbidden reaction

Chart VII



is perturbed by the introduction of a donor level, arbitrarily placed below the important levels of **3** and **7**. We hold the donor at the same distance from C_1 throughout the diagram, thus again allowing the energy term to dominate the perturbation. The analysis is now less straightforward since there are two occupied levels and therefore two chemically significant interactions. The first of these, labeled I, is a stabilizing interaction between the donor orbital and LUMO; the second, II, a net destabilizing interaction between HOMO and the donor orbital. From Chart VII it may be seen that (1) the destabilizing interaction II is greater at the extremes of **3** and **7** than in the transition state for their interconversion, and (2) the stabilizing interaction I conversely is greater in the region of that transition state. Less obvious is the estimate that in the transition-state region the destabilizing

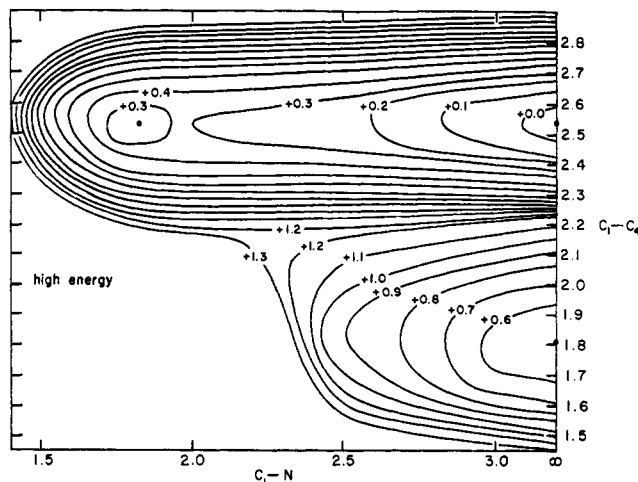


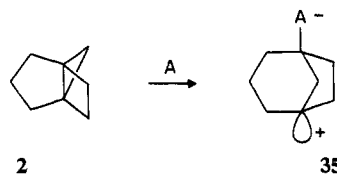
Figure 5. Energy contours in electron volts for the approach of an NH_3 to the tricyclo[2.2.2.0]octane system. The energy zero is arbitrarily chosen at the most stable point. The vertical axis is the $\text{C}_1\text{-C}_4$ distance, the horizontal axis the N-C_1 distance.

interaction II and the stabilizing interaction I roughly cancel each other.²⁸

A less than obvious but logical consequence of the above arguments is that while the relative energy of activation for some given B-C_1 distance can be lower than the same activation energy in absence of base, the absolute value of the activation energy for the interconversion of **3** and **7** cannot be reduced by the intervention of base. An interaction diagram, similar to Chart VI, in which the B-C_1 distance varies, can also be constructed, but is not shown here. It demonstrates that the formation of **34** from **3** must proceed with an activation energy no less than that separating **7** from **3**. These conclusions are confirmed by the contour diagram in Figure 5. Note especially that the approach of the donor does not influence, over a wide range of distances, the energy of the transition state.

The opposite of the reaction which we just examined, namely $\mathbf{34} \rightarrow \mathbf{3}$, is of course the concerted formation of the tricyclo[2.2.2.0]octane *via* an intramolecular $\text{S}_{\text{N}}2$ reaction. The potential surface of Figure 5 indicates a lower activation energy for this direct reaction than for a two-step process through diradical **7**.

The elaborate analysis of the action of acid and base on tricyclo[2.2.2.0]octane makes much simpler the study of the sensitivity of the other tricyclic compounds to such reagents. Consider the reaction $\mathbf{2} + \text{A} \rightarrow \mathbf{35}$.



The coupling of the bridgehead bond stretch with acceptor approach is easily analyzed by writing down the behavior of the energy levels of **2** under $\text{C}_1\text{-C}_5$ stretching (see top of Figure 3; the gap between S and A levels merely decreases) and then perturbing this pic-

(28) It may be noted that the arguments presented here are specific to the situation where the donor level is below the HOMO at all times. This is the situation for all the normal donors we have studied, but exceptions may occur and need to be analyzed separately.

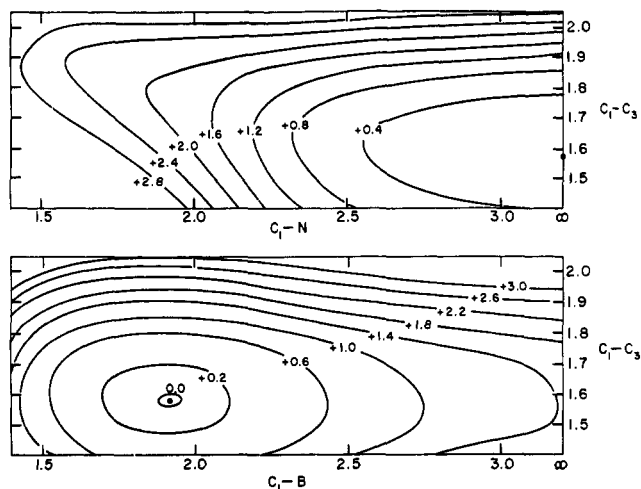
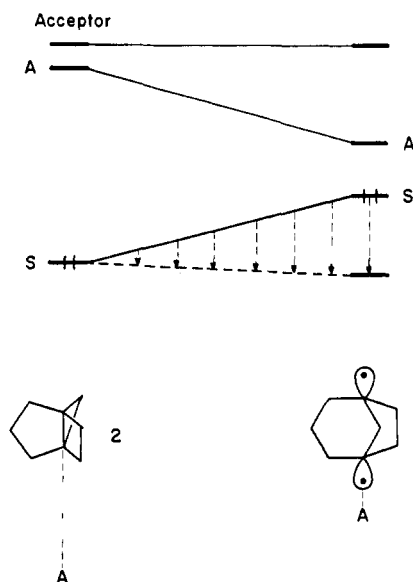


Figure 6. Energy contours in electron volts for the approach of a pyramidal XH_3 to the tricyclo[1.1.1.0]pentane system: $X = N$ is at the top; $X = B$ is at the bottom. In each case the energy zero is at the most stable point. The vertical axis is the C_1-C_3 distance, the horizontal axis the $X-C_1$ distance.

ture by an approaching acceptor. This is done below in Chart VIII.

Chart VIII



The energy of the system is systematically lowered by approach of acid.

The approach of a base, a donor, is analyzed in Chart IX. We see again two interactions: I, stabilizing, and II, destabilizing. Though the energy gap between donor and substrate is greater at right, the extent of interaction is much bigger than at left, because the donor is approaching closer as we move from left to right. Our experience indicates that the repulsive interaction dominates and that the system is destabilized by approach of base.

The final case we analyze is the approach of a radical, as shown in Chart X. The radical attacking level is likely to fall between S and A of substrate, and correspondingly remain at approximately constant energy

Chart IX

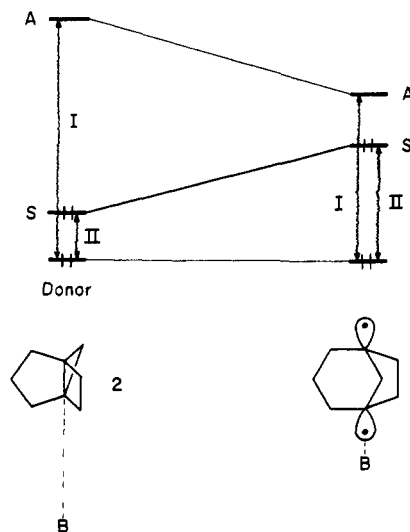
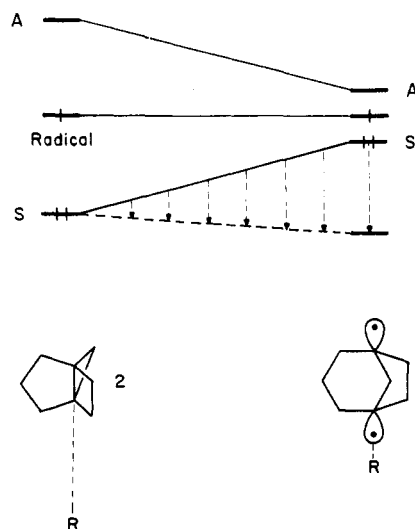


Chart X



throughout the reaction. The tricyclohydrocarbon S level is stabilized and so is the entire system.

We tested our qualitative conclusions with EH potential surfaces for the approach of BH_3 and NH_3 models to the tricyclo[1.1.1.0]pentane (6). The results are presented in Figure 6. Note the easy binding of the Lewis acid and the rise in energy with approach of the base.

We summarize our conclusions: the strained tricyclic hydrocarbons should be stable against base attack, but should react rapidly with acids and radicals. The information at hand for $2^{1a,1b,2,21}$ is consistent with these conclusions.

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