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9. The Stabilization of Bridged Structures of Ethanes

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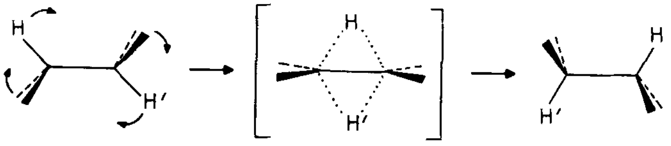
(8. XI. 71)

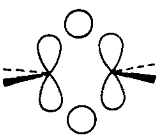
Summary. The source of the instability of D_{2h}, bridged, diborane type geometries of ethanes is traced to a single molecular orbital, b_{2g} or π^* in symmetry. The energy of this orbital can be lowered, and the barrier to bridging accordingly decreased, by appropriately placed acceptor substituents. Low bridging barriers, relative to ethane, are predicted for cyclopentenyl cation, and cyano or nitro substituted ethanes.

Ethane is much more stable in the familiar staggered D_{3d} conformation **1** than in a diborane-like bridged D_{2h} geometry **2**. We consider here the theoretical requirements for preferential stabilization of the bridged form. If sufficient stabilization could be achieved, the bridged structure might serve as an accessible transition state for a novel type of uncatalyzed intramolecular exchange: **1** $\rightleftarrows$ **1′**.



1 **2** **1′**

We first construct the molecular orbitals of **2**, to define those bonding features which cause instability. We start with a pair of in-plane sp^2 hybridized orbitals on



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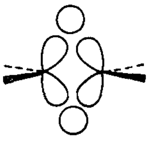

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each carbon, using these to form four normal 'terminal' CH bonds. This leaves one hybrid and a p_π orbital on each carbon atom, and the pair of bridge hydrogen 1*s* orbitals (**3**). Alternately we can mix the p_π and sp^2 hybrid on each carbon to give a pair of equivalent hybrid orbitals (**4**). With either of the two basis sets thus defined we can proceed to a construction of the molecular orbitals. The basis sets generate $2a_g + 2b_{3u} + b_{2g} + b_{1u}$ molecular orbitals, shown schematically in Fig. 1. The rough energy

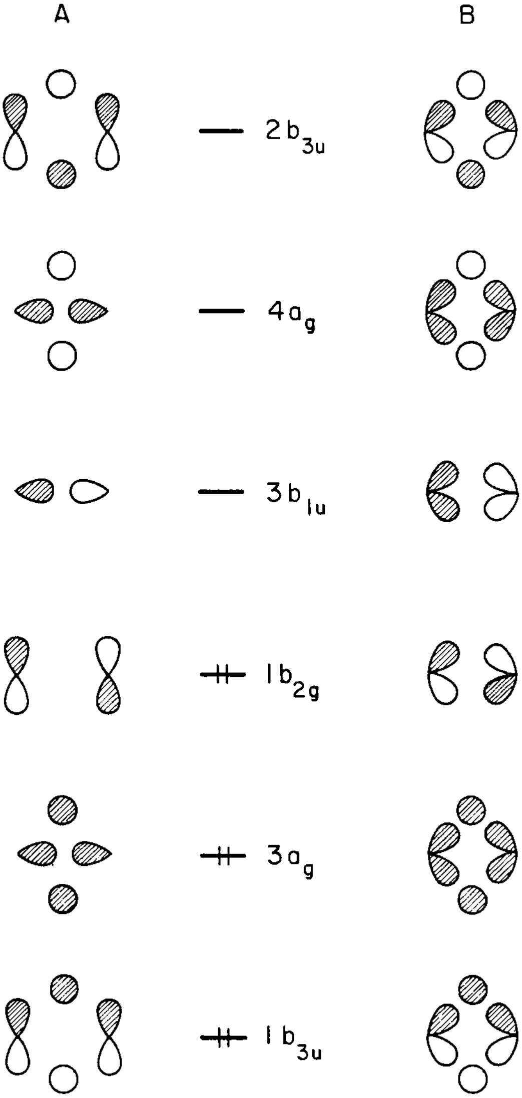
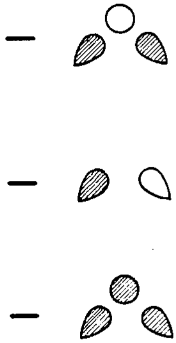


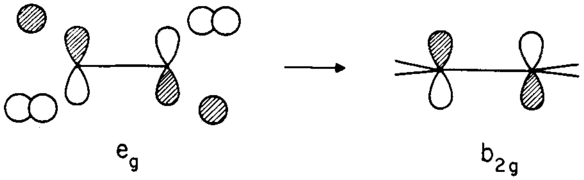
Fig. 1. *Schematic diagram of the molecular orbitals of bridged ethane, omitting the orbitals from the terminal CH bonds*

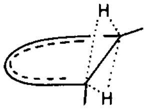
Set A is the representation generated by basis set **3** and set B by **4**. The level ordering is that given by an extended *Hückel* calculation ordering is trivially generated in a number of ways. We could for instance begin with set **4** and form two three-center bonds [1]. Each three-center bond set generates a bonding, nonbonding and antibonding molecular orbital, as shown below.

The 'top' and 'bottom' three-center bond orbitals can then be combined in- and out-of-phase to form set B in Fig. 1. The detailed ordering in energy, for instance why we put $1b_{3u}$ below $3a_g$ rather than above it, is derived from our own semi-empirical calculations1) and the *ab initio* computations of others [3]. The level order may vary with CC distance. The level notation follows the *ab initio* computation convention [3]. Three molecular orbitals are occupied in D_{2h} ethane, since each carbon contributes two electrons and each hydrogen one in our model.



The villain of the piece is the $1b_{2g}$ molecular orbital. Were the two centers far apart, this orbital would be nonbonding. For any reasonable CC distance it is antibonding, and recognizable as the π^* orbital of an ethylene. In both semi-empirical [2] and *ab initio* [3] calculations of the transformation of a staggered ethane into a bridged ethane, the energies of all the orbitals, except one, fall. The one orbital which rises, and does so steeply, is one component of $1e_g$ of D_{3d} ethane, which correlates with the forementioned $1b_{2g}$. In D_{3d} ethane the e_g orbital, while locally exhibiting some CC antibonding, is still a bonding orbital by virtue of positive CH overlap. In the D_{2h} geometry no redeeming CH overlap is allowed by symmetry, while the CC antibonding remains. It is clear that the instability of bridged ethane can be traced to this b_{2g} or π^* level.

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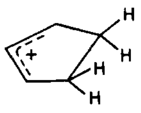
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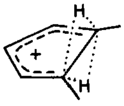
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1) We used extended *Hückel* calculations [2], the hydrogen exponent being set at 1.3.

The most direct approach to stabilizing structures like **2**, then, is to attach substituents, either terminal or on the bridge, which have available low-lying empty orbitals of the proper symmetry to mix with $1b_{2g}$ and depress it in energy. For example we can seek to tie a polyene ribbon in a cyclic manner across the ethane link, as in **5**. The prerequisite for stabilizing interaction is that the lowest unfilled orbital of the polyene possess opposite phase at the carbons adjacent to the ethane, *i.e.* that the polyene LUMO is pseudo-*d*[2]. This is fulfilled by a polyene ribbon with $4q + 2\pi$ electrons. Low bridging barriers are thus predicted for cyclobutene and cycloocta-1,3,5-triene. Our best candidate, however, is obtained by using allyl cation as an acceptor. Fig. 2 shows an interaction diagram illustrating how π^* of bridged ethane is stabilized by LUMO of allyl cation; the resulting structure is the bridged structure **7** of the cyclopentenyl cation **6**.

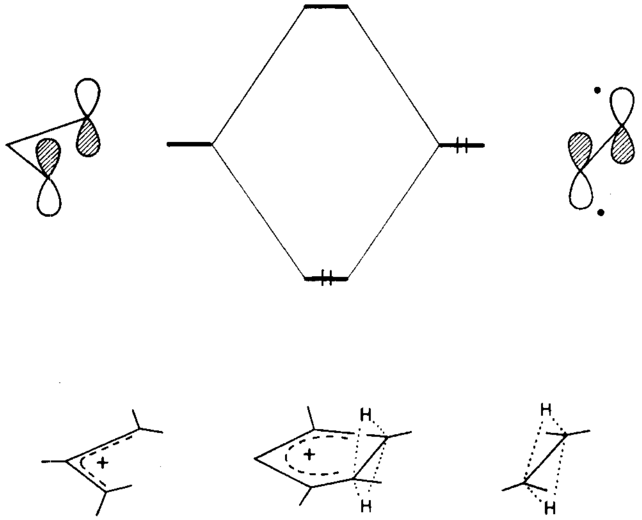

Fig. 2. *Interaction diagram for the nonbonding allyl cation orbital* (left) *mixing with the highest occupied bridged ethane orbital* (right)

We followed the effect of substituents on the bridging activation energy, $\Delta E = E_{\text{bridged}} - E_{\text{unbridged}}$, with semi-empirical molecular orbital calculations of the extended *Hückel* (EH) [2] and CNDO/2 type [5][3]. *Ab initio* calculations [3] give $\Delta E = 8.6$ eV between **1** and **2** unsubstituted. EH yields for the same ΔE 6.7 eV, CNDO/2 7.9 eV. In cyclopentenyl cation, however, bridging costs much less: ΔE for **6** → **7** is 2.6 eV by EH, 1.0 eV from CNDO/2. Though it is not clear which number is more reliable, the anticipated lowering of ΔE is encouraging.

The pseudo-*d* symmetry of the b_{2g} level suggests also the use of an appropriately disposed *d* acceptor orbital. A model compound for this purpose was thiirane (**8**). The b_{2g} or π^* level is in our model calculations certainly stabilized (**9**). However at the same

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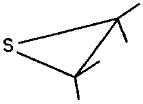
[2] For a definition and application see [4].

[3] The bridge part of the C_2H_6 geometry was optimized, and the resulting bridged CC bond length of 1.65 Å was carried over to other structures. Bridging hydrogen atoms, cyano and nitrogroups were located 0.93, 1.3, and 1.3 Å, respectively, above and below the CC midpoint.

time there takes place a destabilizing interaction, **10**, between the lower π ($1b_{3u}$) orbital and the p-type lone pair on S. For a reasonable choice of S $3d$ parameters, the net effect is a barrier for bridging no smaller than for ethane.



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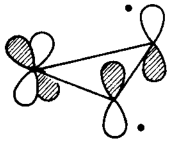

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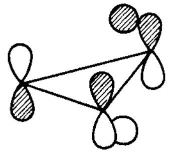

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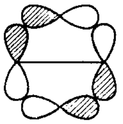
Bridge substitution also offers promise for stabilizing bridged ethanes. The substituent must again provide acceptor orbitals of the proper symmetry to interact with π^* ($1b_{2g}$), for example, as in **11**. An amusing example is provided by two bridging methylene groups. The σ orbitals of the methylenes[4] play the same rôle as the hydrogen 1s orbitals. The methylene p orbitals form combinations of b_{2g} and b_{1u} symmetry, **12** and **13**. These have the correct symmetry to mix with $1b_{2g}$ and $3b_{1u}$ of the bridge framework (see Fig. 1), thus converting two antibonding orbitals into two bonding ones. There are now eight valence electrons to be accounted for, and they all can be accommodated in bonding orbitals. Moreover $3b_{1u}$ is now occupied, and since it is C1–C2 antibonding, that bond is completely broken. Nevertheless a stable bridged structure results. Indeed it is so stable that it is at lower energy than the unbridged structure. For what we have done in a most complicated way is to derive the electronic



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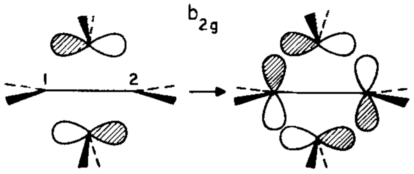

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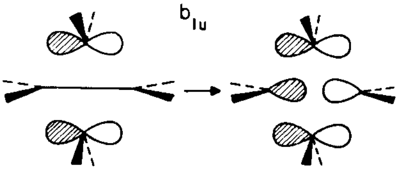

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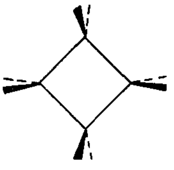
[4] For a discussion of the electronic structure of methylenes see [6].

structure of cyclobutane (**14**), and it is no great surprise that this 'bridged ethane' is more stable than the 'open' tetramethylene (**15**)[5].



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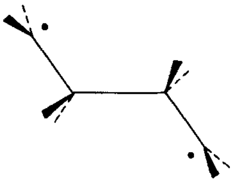

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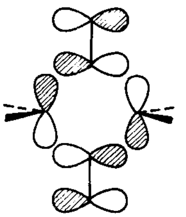
In a more serious vein we consider cyano and nitro groups as bridges. With these substituents we hope for strong interaction of the π^* MO of the bridged ethane with the π-antibonding acceptor orbitals of the substituents, with net electron withdrawal from the CC π^*. The HOMO's of the CN- or NO_2-bridged species should be like **16** and **17**, respectively. ΔE by EH for bridging cyano and nitro are 3.2 eV and 2.2 eV, respectively. CNDO/2 gives 1.9 eV for the latter and surprisingly but no doubt unreliably concludes that 1,2-dicyanoethane prefers a bridged structure to an unbridged one by 0.6 eV.



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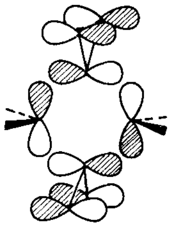

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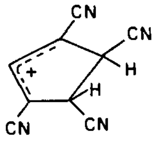
As might be expected, π-acceptors other than polyenes are effective at lowering ΔE when terminally substituted. In tetracyanoethane the EH ΔE to hydrogen bridging is 3.2 eV, for hexacyanoethane 2.5 eV. Four cyano substituents on the cyclopentenyl cation **18** lower the hydrogen bridging barrier to 1.8 eV.



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It should be emphasized that the role of the substituents discussed above is to stabilize the bridged structure by an increase in the number and strength of the bonding interactions found in ethane itself (**2**) and not merely to remove electrons from the π^* orbital of **2**. For *ab initio* calculations on $C_2H_6^{++}$ show that extreme electron withdrawal, without increased compensating bonding, leads not to bridging but to dissociation, without activation energy, into two methyl cation molecules [8].

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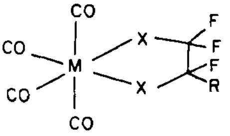
[5] The construction used in the text yields neatly the same cyclobutane orbitals derived in [7].

Our attempts to lower the energy difference between bridged and staggered ethane structures have been qualitatively successful, judging by the numerical experiments we have done. Quantitatively the results are disappointing, in that the effects we have observed are not large. ΔE appears not to have been sufficiently reduced to make observation of the ligand switch $1 \rightleftarrows 1'$ a realistic possibility.

Remarkably, bridged ethane structures have recently appeared in the literature, in systems quite different from those discussed by us. The molecules in question are of type **19**, with M = Mo or Cr, X = $P(CH_3)_2$ or $As(CH_3)_2$, R = H, CF_3 [9]. These ditertiary arsine or phosphine complexes form a structurally related series in which two fluorine atoms, originally occupying quasi-axial position in a puckered chelate ring, shift to more symmetrical positions. Four crystal structures in this series have been reported [9], in the most striking of which, **20**, the fluorine atoms apparently achieve a local bridged ethane structure.



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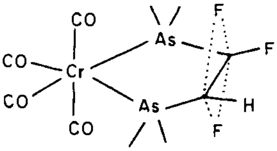

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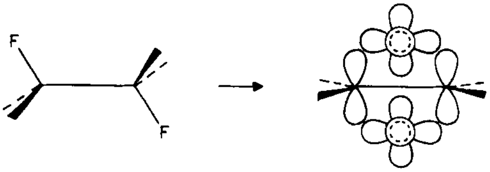
If we ignore momentarily the metal arsine system and consider just the ethane part, we have a model case of bridging fluorine atoms in a difluoroethane, **21**.



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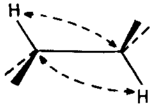
An interaction diagram for the bridged structure can easily be constructed. It reveals no stabilizing features, indeed one antibonding orbital must be occupied. If the metal orbitals and unoccupied arsenic orbitals are included in the calculation, a set of molecular orbitals for **20** can be constructed [9]. However we feel that it contains no extraordinary stabilizing features.

A final, peripheral but interesting observation can be made concerning the bond switching reaction $1 \rightleftarrows 1'$. This process is easily analyzed as a ${}_{\sigma}2_a + {}_{\sigma}2_a$ cycloaddition [10] of two C–H bonds, **22**. As such it is a symmetry-forbidden reaction. It falls into the interesting class of reactions for which the construction of a standard correlation diagram would lead to the misleading conclusion that the reaction is allowed. The



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relevant orbitals for the cycloaddition are shown in Fig. 3. The 'reactant' level labelled a_g on rehybridization and movement of hydrogens takes on the form of 'product' a_g*, reactant a_g* and product a_g having the same relationship. The intended crossing of a_g and a_g* is prevented by the C_{2h} molecular symmetry, but this doesn't make the reaction allowed. We have among the symmetry elements of C_{2h} just those operations which must be carefully watched for to avoid misleading conclusions [11] from correlation diagrams: σ_h is a symmetry element with respect to which all orbitals are symmetric, and C_2 and i do not bisect any bonds made or broken. The $1b_{2g}$ or π* level which we attempted to stabilize in our analysis is the lower component of interacting a_g and a_g*, and owes its high energy to the avoided crossing of these levels.

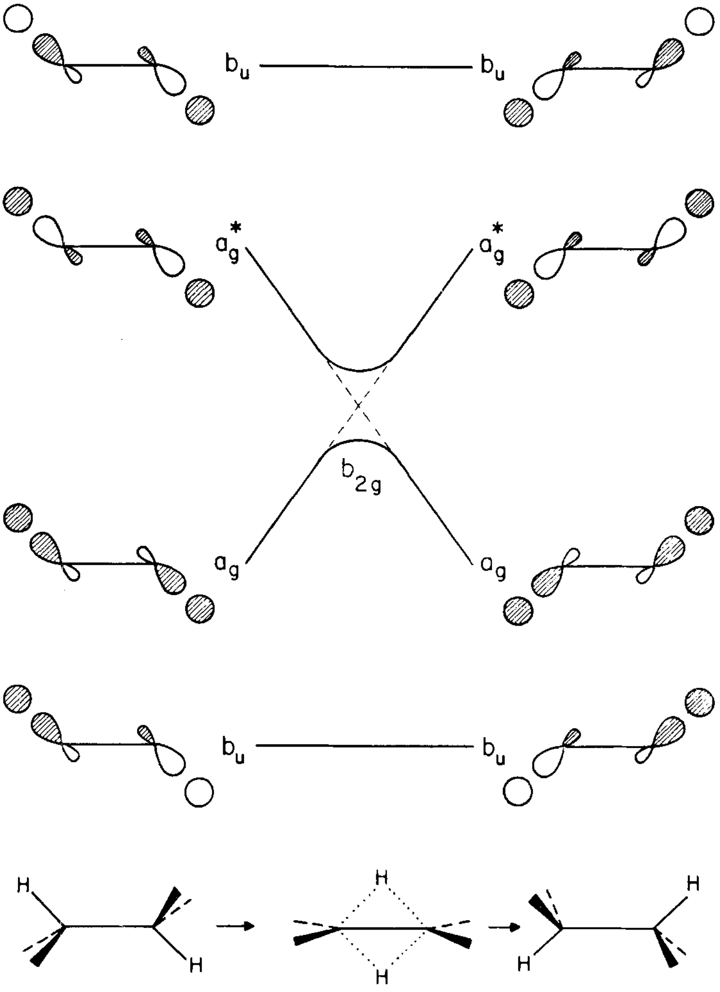

Fig. 3. *Level correlation diagram for the rearrangement* **1** → **1'**

There are in the literature a number of highly interesting reactions where the *formal* overall process is a bond switching 1 ⇄ 1'. Among these are the transformations of santonides [12a], the mutarotation of 5,6-dibromocholestane [12b], some halogen shifts in bicyclic systems [12c], transfer reactions involving boron [12d], and many of the reactions catalyzed by corrinoids. Whether any of these follow a concerted mechanism remains to be established.

We are grateful to the *National Science Foundation* and the *National Institutes of Health* for support of our research. Discussions with *M. T. Reetz*, who has carried out some interesting related work on dyotropic reactions, and with *L. Salem* and *J. D. Dunitz* were of considerable help. The writing of this manuscript was facilitated by the hospitality of the Laboratorium für Organische Chemie der ETH, Zürich, and NSF Senior Postdoctoral Fellowship 51009 to *R. H.*

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10. Synthese der 2-Methyl-lysergsäure Eine neue *Friedel-Crafts*-Methode

74. Mitteilung über Mutterkornalkaloide [1]

von **P. Stütz** und **P. A. Stadler**

Pharmazeutisch-chemische Forschungslaboratorien *SANDOZ AG*, Basel

(9. XI. 71)

Summary. The new reagent 2-methoxy-1,3-dithiolane and cyclic ortho-thioesters can be used in a new reaction of the *Friedel-Crafts* type to introduce the corresponding aldehydic or ketonic thioacetal function directly into substrates containing an indole nucleus with free 2- or 3-position.

Von den Substitutionen in Stellung 2 des Lysergsäure-Grundgerüstes sind bisher die Einführung einer Halogenfunktion [2] und einer Nitrofunktion, letztere jedoch nur