shorter time; products, **2g** and **2h**) after 42% conversion no racemization of **1g** was observed. Similarly with the optically active **1k** (Pyrex) no racemization was observed after 24% conversion.[17] Clearly the δ process, occurring at short wavelength only, does not involve a comparatively long-lived biradical capable of reversion to starting material, as has been observed in the analogous type II reactions.[4] On the other hand the γ process, occurring at long wavelength, may well be of this type.

The evidence described requires that a higher excited state of an aromatic thione be long-lived enough for chemical reactivity to compete with photophysical processes. That such is possible has already been demonstrated for thiobenzophenone (S_2; $\tau \sim 10^{-11}$ sec) an upper state of which exists long enough for intermolecular reaction;[18] such phenomena may be a consequence of the large S_1–S_2 separation. Efficient intersystem crossing ($S_1 \leadsto T_1$), as indicated by the observation of phosphorescence excludes the possibility of S_1 and T_1 being the two reactive states.

(17) The expected cyclopentanethiol from this irradiation has been characterized. The stereospecificity of its formation is being studied.

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(19) Holder of a "Fundacion Juan March" Fellowship (Spain) 1972–1973.

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MINDO/3 Study of the Thermal Conversion of Cyclobutene to 1,3-Butadiene[1]

Sir:

While various qualitative arguments[2-6] lead to the prediction that the thermal ring opening of cyclobutene (**1**) to 1,3-butadiene (**2**) should take place preferentially in a conrotatory manner, a more quantitative treatment is needed to establish the nature of the transition state and the difference in activation energy between the "allowed" conrotatory and "forbidden" disrotatory processes.

In our preliminary studies,[7] using MINDO/2,[8] we established the unusual form of the disrotatory potential surface, this having the "two-valley" structure characteristic[7c] of "forbidden" pericyclic reactions, and also that the conrotatory transition state is nonplanar.[9]

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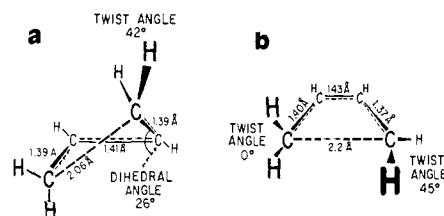
Figure 1. Calculated geometry for transition state for (a) conrotatory and (b) disrotatory interconversion of cyclobutene and 1,3-butadiene.

The nonplanarity of the transition state was subsequently confirmed by an *ab initio* calculation by Buenker, *et al.*[10]

While we[7] and Buenker, *et al.*,[10] also arrived at estimates for the differences between the activation energies for the two pathways, both of these were open to criticism in that assumptions were made concerning the geometry of the disrotatory transition state. We have now reinvestigated the problem using a recently improved version of MINDO (MINDO/3[11]) together with a much superior geometry program[12] which enabled us to study both reaction paths in detail without the need for simplifying assumptions.

The conrotatory transition state was first located approximately by using the length (r) of the breaking bond as reaction coordinate,[7] and the exact structure was then determined by a procedure,[13] analogous in principle to that of McIver and Komornicki[14] based on a minimization of the scalar gradient of the energy. The final structure (Figure 1a) agrees closely with those predicted by MINDO/2[9] and by the *ab initio* calculation of Buenker, *et al.*[10] The calculated activation energy (49.0 kcal/mol) is too large (obsd 36 kcal/mol[15]), a surprising discrepancy since MINDO/3 calculations for a number of other pericyclic processes have given activation energies that are within ±5 kcal/mol from experiment. The *ab initio* SCF calculations of Buenker, *et al.*,[10] gave a predicted activation energy of 65 kcal/mol without CI,[16] reduced to 48.8 kcal/mol[10] by inclusion of extensive CI.

All previous studies (*e.g.*, ref 7 and 10) of the disrotatory opening of **1** to **2** have assumed that symmetry is retained throughout, *i.e.*, that the two methylene groups rotate at the same rate. Some restraint must of course be imposed to force the reaction to follow a disrotatory path but this is unnecessarily severe. It was made necessary in the earlier calculations[7,10] by the need to reduce the number of independent variables. Since the calculation of geometries for systems of this

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size using MINDO/3 and without making any assumptions, is now trivial,[12] we were able to impose a less rigorous constraint on the system to enforce disrotatory reaction. We assumed only that as one of the methylene groups in **1** rotates, the other is prevented from rotating in a conrotatory sense, being, however, free to rotate disrotatorily. Under these conditions the reaction followed a course entirely different from that[7,10] previously assumed, involving the formation of the orthogonal biradical **3**. The transition state of the reaction lies between **1** and **3**, its structure (Fig. 1b) corresponding to rotation of one of the methylene groups in **1** through 45° while the other remains orthogonal to the C_4 plane. All previous calculations for the reaction must therefore be disregarded. The calculated activation energy (55.6 kcal/mol) leads to an estimate of the difference between the conrotatory and disrotatory paths of 16.6 kcal/mol, in good agreement with a recent experimental estimate ($\geq$15 kcal/mol[17]).

The reaction therefore follows the pattern predicted by our recent discussion[6] of the course of "forbidden" reactions in terms of orbital isomerism. Such a reaction involves the interconversion of lumomers and must therefore involve an orbital crossing and an intermediate biradical. The reaction will try to cross the biradical barrier at its lowest point, *i.e.*, one corresponding to the most stable form of the biradical. Here that would be expected to be **3** since any interaction between the in-plane 2p AO and the MO's of the allyl moiety will be antibonding.[4]
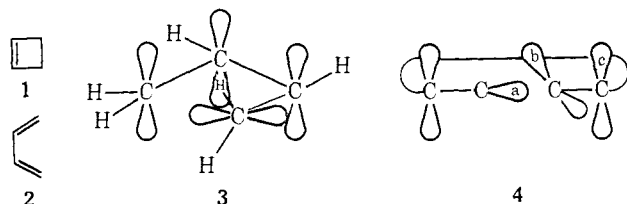
It is easy to see why an energy barrier should separate **1** from **3**. As one of the methylene groups in **1** begins to rotate, the interaction between the AO's (a and b in **4**) forming the H_2C–CH_2 bond in **1** decreases. Initially the resulting decrease in energy is not compensated by the nascent interaction between the AO (b) of the rotating methylene and the 2p AO (c in **4**) of the adjacent olefinic carbon atom. As the reaction proceeds, the latter interaction becomes progressively more important and so at some point the effect of bond formation outweighs that of bond breaking. The energy of the system would therefore be expected to rise to a maximum in the vicinity of a twist angle of 45° and then to decrease again. This is exactly what we find.

These results stress once more the categorical need for complete geometry optimization in calculations of reaction paths. Calculations in which assumptions are made concerning the geometries of the intermediate phases are worthless and can be very misleading.

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## The Pyridyl Unit in Host Compounds[1]

Sir:

Multiheteromacrocycles that contain as part of the major ring 2,6-disubstituted pyridine units have been reported combined with just CH_2CH_2 units,[2a,b] just CH_2SCH_2 units,[2c] just CH_2SCH_2 combined with CH_2O–CH_2 units,[2d] and just CH_2OCH_2 combined with o-CH_2-$C_6H_4CH_2$ units.[2e] The ability of crown ethers to bind cations[3] stimulated the design of cyclic polyethers that as host compounds formed highly structured molecular complexes with appropriate guest compounds.[4] We report here the feasibility of introducing into host compounds pyridyl units, which act as binding and shaping sites for specific guest compounds.

Treatment of **1**[5] with hydrobromic acid at 120° (1 hr) gave, after neutralization, extraction, and chromatography, 39% recovered **1**, 16% of **2**,[2a] and 41% of
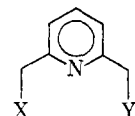
1, X = Y = OH; 2, X = Y = Br; 3, X = Br, Y = OH;
4, X = OH, Y = H; 5, X = Cl, Y = H; 6, X = Y = Cl
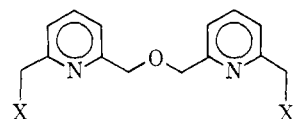
7, X = H; 8, X = OAc; 9, X = OH

3,[6a,b,c,e] mp 74–78° (dec). In tetrahydrofuran at 25°, **4**[2a] was metalated with sodium hydride, and then treated with **5**[2a] to give (74%) **7**,[6a,b,c,d] mp 77–78°. Ether **7** in glacial acetic acid–30% hydrogen peroxide at 80° (14 hr) gave (85%) crude bis(N-oxide),[6b] mp 161–173°, which was heated in acetic anhydride[5] at 100° (9 hr) to give (17%) after chromatography and crystallization, **8**,[6a,b,d] mp 97–98.5°. Hydrolysis of **8** with sodium hydroxide gave (90%) crude **9**.[6b]

Treatment of **1** with tetraethylene glycol ditosylate in refluxing tetrahydrofuran, potassium *tert*-butoxide, and 2.5% water gave (29%) after chromatography and

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