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Bridged Radical Intermediates of Aryl [1,2] Rearrangements

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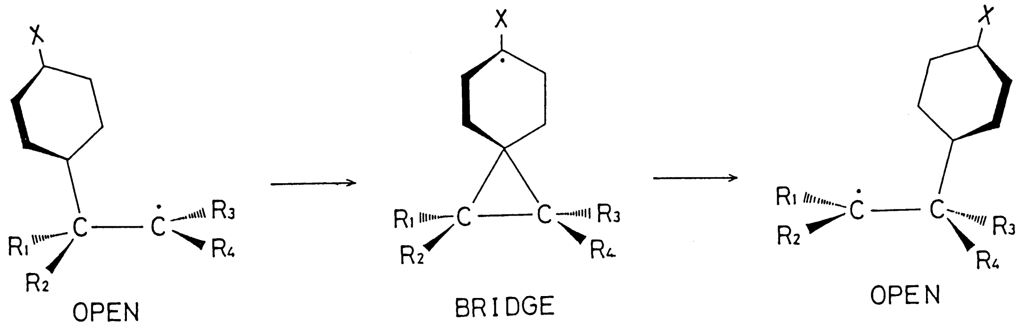
Bridged-form free-radical intermediates are calculated to be present in the course of aryl [1,2] sigmatropic rearrangements. The geometry of cyclopropane rings involved in intermediates is not affected by substituents.

Aryl and some unsaturated groups are known to migrate sigmatropically.1) Compared to rearrangements of cationic species, those of radical intermediates have not been clarified satisfactorily due to the rapid occurrence of other reactions such as hydrogen abstraction. There is a fundamental mechanistic question of whether the bridged intermediate is at the transition state (TS) of the migration or is the stable detectable species.



To examine structure and energy of the intermediate, we perform an *ab initio* MO calculation using the STO-3G basis set implemented in the GAUSSIAN 82 program.2)

In Fig. 1a, optimized geometries of classic open form (OPEN) and non-classic bridged form (BRIDGED) are shown. In BRIDGE, cyclopropane ring with the spiro carbon is formed, and the spin density is delocalized in the benzene ring. BRIDGE is obtained to be a stable equilibrium structure through vibrational analysis (all the harmonic frequencies are real). TS of the

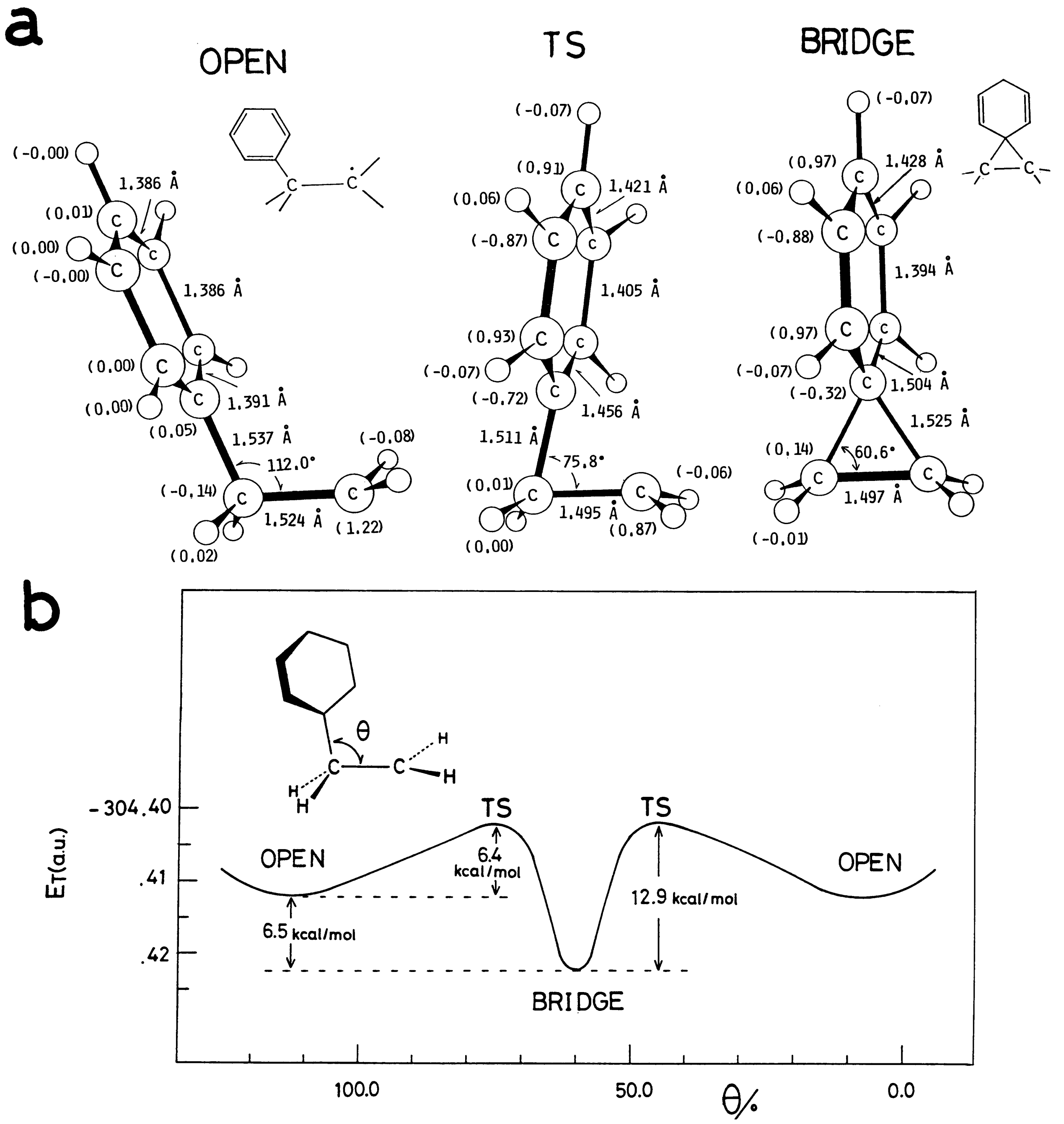


Fig. 1 a. Geometries ($x=R_1=R_2=R_3=R_4=H$) of OPEN, TS and BRIDGE determined with the UHF STO-3G method. OPEN and TS are of the C_s symmetry and BRIDGE is of C_{2v}. Numbers in parentheses denote the atomic spin densities. Empty circles stand for hydrogen atoms.

b. The potential energy of the phenyl migration. 1 a.u. = 1 hartree = 627.52 $\mathrm{kcal \cdot mol^{-1}}$.

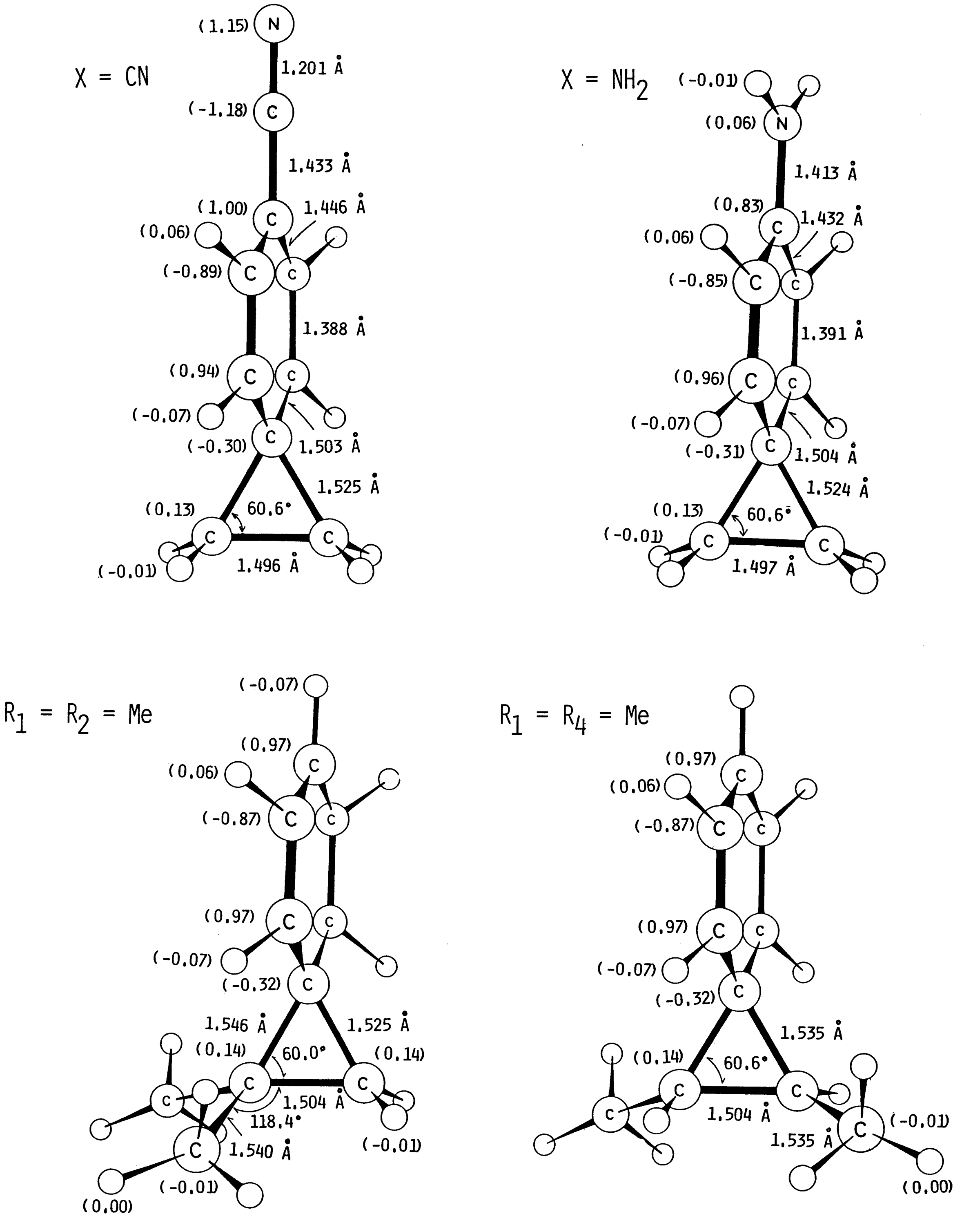


Fig. 2. Stable BRIDGE forms at aryl migration. At R_1=R_2=Me and R_1=R_4=Me, the benzene ring is fixed to that of BRIDGE in Fig. 1a during the geometry optimization.

(OPEN → BRIDGE) is sought and is shown also in Fig. 1a. Figure 1b gives an energy diagram of the phenyl migration. Although BRIDGE is the most stable species in the UHF MO, the energy barrier of isomerization is not so large as to make BRIDGE isolated in "aggressive" radical chain reactions. In addition, the UHF method with the spin contamination overestimates the stability of BRIDGE.[3] The ROHF calculation is also made on the UHF geometry[4] to give the stability order, OPEN(0 $kcal\cdot mol^{-1}$) > BRIDGE(30) > TS(46). In view of the UHF-ROHF difference, in reality, OPEN would be stable comparably to BRIDGE.

Figure 2 gives substituent effect on the BRIDGE geometry. Electron withdrawing and donating groups are attached to the *para* position. In other two BRIDGE's two methyl groups are attached to the ethylenic moiety. The shape of the cyclopropane ring is almost insensitive to these substituents. That is, BRIDGE seems to be a stable intermediate irrespective of the substituent. The stability arises from the valence isomerism. BRIDGE cannot be stable in cases where no such isomerism is possible. For instance, in the methyl-radical [1,2] migration ($H_3C\text{-}CH_2CH_2^{\bullet} \rightarrow {}^{\bullet}CH_2\text{-}CH_2\text{-}CH_3$), BRIDGE corresponds to TS with a large energy barrier (97.2 $kcal\cdot mol^{-1}$).

This theoretical work suggests that the bridge-form radical intermediate is basically detectable during the aryl migration and the geometry of the intermediate is not susceptible to the substituent.

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References

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3) D. J. Pasto, J. Am. Chem. Soc., 110, 8164 (1988).

4) The UHF optimized geometry is similar to the ROHF one. For instance, C-C lengths of the D_{6h} benzene cation radical ($C_6H_6^+$) are 1.403 Å(UHF) and 1.400 Å(ROHF), respectively.

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