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A THEORETICAL STUDY OF THE ISOMERIZATION PROCESS IN TRIS(2-THIENYL)METHYL RADICAL

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Abstract—An INDO study has shown that the title compound exists in two diastereomeric propeller-like conformations, a *cis* form (C_3 symmetry), and a *trans* form (C_1 symmetry). The *cis* form is more stable than the *trans* form by 0·75 kcal/mole. The two forms undergo ready conformational interconversion by the two-ring flip mechanism, with activation energies of *ca.* 6 kcal/mole.

INTRODUCTION

The conformational properties of several radicals containing the thiophene ring have been the subject of recent investigations.[1-3] In a number of cases different ESR signals from distinct conformational isomers could be detected and their stereochemistry assigned. These include the radical anions of biaryls,[1] and some ketyl[2] and nitroxide radicals.[3] On the other hand, attempts in this direction were unsuccesful on a number of trithienylmethyl radicals,[4] which may also exist in different conformations, as no line broadening or separation of ESR lines due to non-equivalent species could be observed in the temperature range compatible with their stability. Two reasons may be responsible for this behavior: (i) the energy difference between one isomer and the other ones is so large (>1 kcal/mol) that only one is being observed under all conditions, (ii) the energy barrier to isomerization is too small to allow the internal rotation of the thiophene rings to be frozen out on the ESR time scale. An upper limit for this barrier should be *ca.* 8–9 kcal/mol considering that variable temperature studies could be made only above *ca.* 15–20°; below this temperature the radicals dimerize. To decide between these two alternatives we undertook a theoretical study on tris(2-thienyl)methyl radical (**1**).

RESULTS

For the purpose of this investigation, i.e. a detailed analysis of the isomerization process of **1**, we chose to employ the INDO method, since it had already been shown that this computational procedure provides reliable results in conformational studies of radicals.[5] All the calculations were carried out with an INDO program parametrized for second row elements according to Benson and Hudson.[6] In all the computations reported in the present paper, the geometrical parameters for the three thiophene rings were kept fixed to values reported for 2,2′-bithienyl.[7]

It was found that **1** exists in two propeller-like diastereomeric *dl* forms, a *cis* form (*A*) of C_3 symmetry, and an asymmetric *trans* form (*B*), and that *A* is more stable than *B* by 0·75 kcal/mol.

The energy of *A* was minimized with respect to the bond distances $r(C_m–C_r)$ between the methyl carbon (C_m) and the carbon of the ring (C_r), and with respect to the twist angle ϑ, i.e. the dihedral angle between the reference plane (defined by the three C_r atoms) and the plane of the thiophene ring. The three dihedral angles were varied by the same amount because of symmetry. The computed values are: $r(C_m - C_r) = 1{\cdot}434$ Å and $\vartheta = 25{\cdot}5°$. The energy of *B* was also optimized with respect to $r(C_m - C_r)$ and with respect to the three dihedral angles. It was found that the optimum conformation is that with $\vartheta_1 = \vartheta_2 = \vartheta_3$: *ca.* 26° (relative to $\vartheta = 0°$ for the planar C_s conformation). In these calculations, all three bond angles $C_rC_mC_r$ were kept fixed arbitraly at 120°.

Although, for reason of symmetry, the central carbon atom, C_m, in *A* and *B* is expected[8] to be displaced from the reference plane by a finite even if small amount (i.e. to be slightly pyramidal), our calculations indicate that the displacement is negligible in magnitude. Thus, if C_m in *A* is displaced along the C_3 axis to form a pyramidal array $C_m(C_r)_3$, the energy increases by *ca.* 2·8 kcal/mol when C_m is displaced by 0·125 Å (corresponding to $C_rC_mC_r = 119{\cdot}25°$) in the direction toward the sulfur atoms and by *ca.* 2·15 kcal/mol when the displacement is to the same extent in the opposite direction. Consequently, C_m may for all practical purposes be considered to lie in the reference plane.

The various transition states occurring in the isomerization processes were all optimized with respect to $r(C_m - C_r)$. In this optimization, bond distances to a C_r belonging to a planar or a perpendicular ring (with respect to the reference plane) were treated independently and are denoted by r_p and r_v, respectively. The corresponding computed values, with reference to Fig. 1, are: (i) $r_p = 1{\cdot}45$ Å for the planar transition states C and D occurring in the zero ring flip; (ii) $r_v = 1{\cdot}45$ Å for the transition states J and K occurring in the three ring flip; (iii) $r_p = 1{\cdot}435$ Å and $r_v = 1{\cdot}445$ Å for the transition states E, F, G involved in the one-ring flip. In the two diastereomeric transition states occurring in the two-ring flip, H and I, $r_v = 1{\cdot}448$ Å in H and I, and $r_p = 1{\cdot}422$ Å in H and $1{\cdot}442$ Å in I. In all of these computations, the three bond angles $C_rC_mC_r$ were kept fixed arbitrarily at 120°.

DISCUSSION

In the stereoisomerization processes referred to in Table 1, zero, one, two or three 2-thienyl rings "flip", i.e. rotate about their respective C_m–C_r bonds through planes

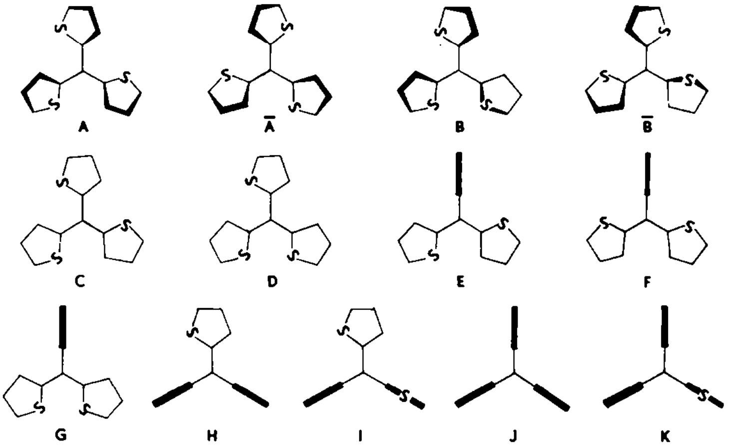

Fig. 1. The two propeller-like diastereomeric *dl* forms of tris(2-thienyl)methyl radical (*A* and *B*), together with the various diastereomeric transition states occuring in the isomerization processes.

Table 1. Summary of flip processes for tris(2-thienyl)methyl radical (**1**)

Flip Process	Interconverting Conformers	Activation Energy (kcal/mol)	Transition State[c]
Zero-ring	$A \rightleftarrows \bar{A}$	22.8	C
	$B \rightleftarrows \bar{B}$	25.1	D
One-ring	$A \rightleftarrows \bar{B}$[a]	9.6[b]	E[d]
	$B \rightleftarrows \bar{B}$	9.4	F
		11.7	G
Two-ring	$A \rightleftarrows \bar{B}$[a]	6.5[b]	H[d]
	$B \rightleftarrows \bar{B}$	5.7	I[d]
Three-ring	$A \rightleftarrows \bar{A}$	17.9	J
	$B \rightleftarrows \bar{B}$	17.2	K

[a] Or $\bar{A} \rightleftarrows B$. [b] From A to $\bar{B}$ or from $\bar{A}$ to B. [c] Optimized with respect to *r*. The geometry of the thiophene ring was not allowed to change. C_m and the three adjacent carbon atoms C_r were constrained to remain in the same plane. [d] Only one of the two enantiomeric transition states is shown in Figure 1.

perpendicular to the reference plane, while the remaining rings rotate in the opposite direction, through the reference plane. The conformational dynamics of **1** are strictly analogous (except for numerical values of energy barriers) to those of the stereochemically correspondent[9] tris-1-(2-methyl-naphthyl)borane (**2**),[10] which also exists in diastereomeric *cis* (C_3) and *trans* (C_1) forms; the reader is referred to this paper[10] for fuller details. In both **1** and **2**, zero or three-ring flips interconvert only enantiomers ($A \rightleftarrows \bar{A}$ or $\bar{B} \rightleftarrows B$). The energy of the zero- and three-ring flips is substantially higher than those of the one- and two-ring flips because of severe nonbonded interactions in the transition state.[11] In both **1** and **2**, interconversion of B and B̄, but not of A and Ā, can take place in a single step by either a one- or a two-ring flip. In both **1** and **2**, interconversion of A and B̄ (diastereomerization), and of Ā and B, is possible in a single step, and A and Ā may thus be enantiomerized by three-step processes, i.e. $A \rightleftarrows \bar{B} \rightleftarrows B \rightleftarrows \bar{A}$.

A distinction between one and two-ring flips is that in the former, enantiomerization of B and B̄ may proceed via two diastereomeric transition states, which differ in energy, whereas in the latter the two possible transition states for the interconversion of B and B̄ are enantiomeric and thus are the same in energy.

As revealed by our calculations (Table 1) the two-ring flip is the preferred pathway for the interconversion of the conformers of **1**.

Experimental studies[12] and force field calculations[13] had previously shown that in a great variety of compounds containing three aromatic rings bonded to a common central atom, the pathway of lowest energy for the interconversion of right- and left-handed propellers is, without known exception, the two-ring flip mechanism.[11] The present case is thus in full accord with this generalization. Given the low energy barrier to interconversion ($A \rightleftarrows B$, 6·5 kcal/mol) line broadening effects can probably be observed in the ESR spectrum only at temperatures below those at which dimerization of the radical occurs.

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