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Theoretical Study of Thieno[3,4-*c*]thiophene, a Nonclassical Thiophene System

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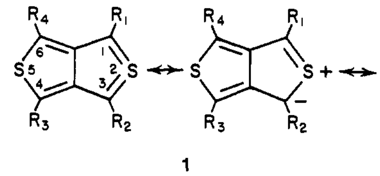
Abstract: The reaction of thieno[3,4-*c*]thiophene with dicyanoacetylene is examined as a model for cycloadditions of derivatives of this ring system with dipolarophiles utilizing the MINDO/3 approximation in MO theory. Extrusion of elemental sulfur as an atomic species from the initial 1:1 cycloadduct is shown to be energetically unfavorable, whereas formation of elemental sulfur (S_6 or S_8 species) results in a favorable energy change for the overall reaction. A mechanism for the extrusion of sulfur is suggested which involves a novel thiirane species that dimerizes to a disulfide which in turn decomposes to give the expected product, 5,6-dicyanobenzo[*c*]thiophene, and an intermediate that ultimately allows for the extrusion of S_6 or S_8. The stability of 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene is found to result from steric effects. Reactions at the 1, 3, 4, and 6 positions are inhibited by steric constraints except for small molecules such as oxygen. However, increased temperatures, resulting in a more rapid rotation of the aryl substituents, increase the likelihood of approach to these positions and of a reaction with sterically more demanding dipolarophiles. Theoretically determined rotational barriers for the aryl substituents are in good agreement with data obtained from NMR studies on 1-(1,1-dimethyl-6-indanyl)-3,4,6-triphenylthieno[3,4-*c*]thiophene prepared from 3-benzoyl-4-(1,1-dimethyl-6-indanoyl)-2,5-diphenylthiophene and P_4S_{10}.

Introduction

The thieno[3,4-*c*]thiophene system **1**, a 10 π-electron heteropentalene containing a nonclassical thiophene nucleus, is of synthetic and theoretical interest.[1-4] The synthesis of thieno[3,4-*c*]thiophene (**1a**) itself has not been reported, but derivatives of **1** having aryl substituents in the 1, 3, 4, and 6 positions are isolable. 1,3-Dimethylthieno[3,4-*c*]thiophene (**1b**) and 1,3-dicarbomethoxythieno[3,4-*c*]thiophene (**1c**), however, could not be isolated, but they were characterized by their 1:1 cycloadducts formed with *N*-phenylmaleimide.[5]



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a, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = R_2 = CH_3; R_3 = R_4 = H$
c, $R_1 = R_2 = COOCH_3; R_3 = R_4 = H$
d, $R_1 = R_2 = R_3 = R_4 = C_6H_5$
e, $R_1 = R_4 = C_6H_5, R_2 = R_3 = H$
f, $R_1 = p\text{-}C_6H_4OCH_3; R_2 = R_3 = R_4 = C_6H_5$

1,3,4,6-Tetraphenylthieno[3,4-*c*]thiophene (**1d**) undergoes cycloaddition with several electron-deficient olefinic[5] and acetylenic[6,7] dipolarophiles. With the former, both the exo and endo cycloadducts are obtained; with the latter, the initial 1:1 cycloadduct is not isolated as it readily extrudes sulfur to give the corresponding benzo[*c*]thiophenes. Photooxidation of **1d** proceeds very rapidly in solution[5] and is also observed to occur gradually at the crystal surface.[8]

Early molecular orbital calculations using the semiempirical PPP-SCF-MO method,[9] which ignores d-orbital interactions, predicted a triplet ground state for **1a**. A subsequent investigation based on the photoelectron spectrum of **1a** with an unrestricted version of the extended CNDO/S method predicted that the triplet was more stable than the closed-shell singlet state by 1.4 kcal mol^{-1}. With configuration interaction (CI) and incorporation of the d orbitals, the lowest singlet emerged 31.8 kcal mol^{-1} more stable than the lowest triplet state.[10] A recent study[11] based on the photoelectron, ESR, and electronic absorption spectra of **1d** supports the prediction of a singlet ground state and indicates that the most appropriate representation of the π system consists of

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[1] Abstracted in part from the Ph.D. thesis of Karl F. Moschner, Rensselaer Polytechnic Institute, 1981.

[2] Potts, K. T. "Special Topics in Heterocyclic Chemistry"; Weisberger, A., Taylor, E. C., Eds.; Wiley: New York, 1977; Chapter 6. Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *7*, 139–144.

[3] Cava, M. P. *Int. J. Sulfur Chem.* **1972**, *C7*, 55–59.

[4] Ramsden, C. A. *Tetrahedron* 1977, *33*, 3203–3232.

[5] Cava, M. P.; Pollack, N. M.; Dieterle, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 2558–2560.

[6] Cava, M. P.; Behforouz, M.; Husbands, G. E. M.; Srinivasans, M. *J. Am. Chem. Soc.* **1973**, *95*, 2561–2564.

[7] Potts, K. T.; McKeough, D. *J. Am. Chem. Soc.* **1974**, *96*, 4268–4275.

[8] Potts, K. T., unreported observations.

[9] Clark, D. T. *Tetrahedron* **1968**, *24*, 2567–2573.

[10] Müller, C.; Schweig, A.; Cava, M. P.; Lakshmikantham, M. V. *J. Am. Chem. Soc.* 1976, *98*, 7187–7189.

[11] Gleiter, R.; Bartetzko, R.; Brähler, G.; Bock, H. *J. Org. Chem.* **1978**, *43*, 3893–3897.

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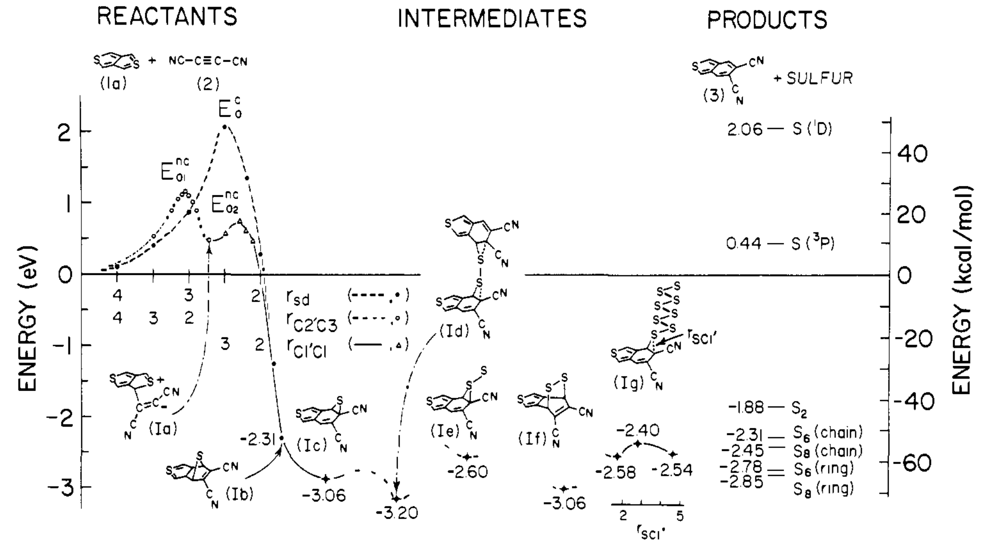


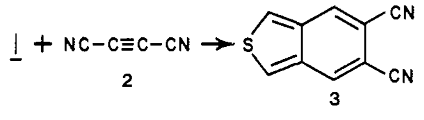
Figure 1. Theoretical reaction surface for the cycloaddition reaction of thieno[3,4-*c*]thiophene (**1a**) with dicyanoacetylene (**2**) to yield 5,6-dicyanobenzo[*c*]thiophene (**3**). Energies for the hypothetical intermediates and possible products are reported as per mole of atomic sulfur of the chain or ring units.

the various dipolar species implicit in **1**. The present calculations using MINDO/3 MO theory,[12] which does not consider d-orbital interaction, also predict a singlet aromatic ground state for **1a** when CI is included. This singlet state is much more stable than the lowest triplet state.

The ready addition of oxygen to **1d** either in solution[5] or more slowly at the crystal surface,[8] is consistent with the very small steric restraint to the addition of oxygen across the thiocarbonyl ylide dipole. The oxygen molecule is almost small enough to be accommodated between the two phenyl substituents at positions 1 and 3 of **1d** regardless of the orientation of these groups. The initial adduct is assumed to be a thio-ozonide which undergoes ready decomposition to a mixture of ketone, thioketone, and thioketone oxide products.[5]

In contrast, **1d** reacts relatively slowly in boiling inert solvents with electron-deficient olefinic[5] and acetylenic[6,7] dipolarophiles. With the latter dipolarophiles, the initial cycloadduct is not isolated, the product obtained being that formed by extrusion of sulfur from the initial 1:1 cycloadduct.

Our study addresses several questions of interest. Why are the tetraaryl derivatives the only examples of this ring system that have been isolated; and, what is the nature and mechanism of the sulfur extrusion? This investigation considers the hypothetical reaction of **1a** with dicyanoacetylene (**2**) to yield 5,6-dicyanobenzo[*c*]thiophene (**3**). The reaction is shown in Figure 1 along with some of the proposed intermediates, denoted by Ia, Ib, Ic, etc.



The S-bridged intermediate Ib has been traditionally used in an operational mechanism.[1,5,7] Based on the energy of products, atomic sulfur cannot be extruded from it. It will be shown that the energy of the thiirane Ic favors it as an intermediate species in the cycloaddition and the starting point in the successive reactions which yield a sequence of intermediates including S_2 through S_8 units (Id–g). Cost restraints prohibit examination of all reaction pathways, but, because the best of those examined are close in energy, several are suggested to demonstrate that extrusion of some form of elemental sulfur other than atomic sulfur is favored energetically from the hypothetical intermediates. Formation of ^1D and ^1S states of atomic sulfur is not favored relative to the reactants **1a** and **2**, and the symmetry-forbidden ^3P state also lies above the reactants. To perform these calculations, the MINDO/3 program was adapted to the IBM 3033 in double precision and modified to remove oscillations and to force convergence.[13]

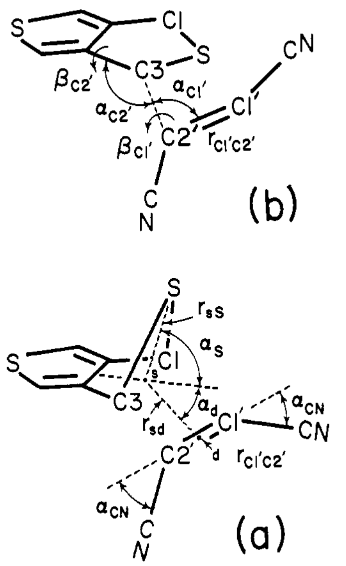


Figure 2. Reaction coordinates for (a) concerted and (b) nonconcerted cycloaddition reactions.

The Model Reaction

The theoretical approach requires species which contain the essential features of the reactants while retaining structural simplicity required for computation. The reaction surface of **1a** with dicyanoacetylene (**2**), has been examined by selecting an appropriate reaction coordinate shown in Figure 2. These were systematically varied while allowing bond and torsional angles to achieve a minimum energy configuration. As there is no general consensus regarding the mechanism of cycloaddition reactions from experimental mechanistic studies[14-17] or theoretical calculations,[18-22] both concerted and nonconcerted paths were investigated

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(12) See, for example: Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285–1293.

(13) Miller, K. J.; Pycior, J. F.; Moschner, K. F. *QCPE Bull.* **1981**, *1*, 67–70.

(14) Firestone, R. A. *Tetrahedron* 1977, *33*, 3009–3039.

(15) Huisgen, R. *J. Org. Chem.* 1976, *41*, 403–419.

(16) Bartlett, P. D. *Q. Rev. Chem. Soc.* **1970**, *24*, 473–497.

(17) Sauer, J. *Angew. Chem., Int. Ed. Engl.* 1967, *6*, 16–33.

by varying the respective coordinates illustrated in Figures 2a and 2b. All calculations, except when otherwise indicated, are of ground-state singlets.

For the *concerted* reaction path, the acetylenic carbon atoms were allowed to approach the reaction sites at positions 1 and 3 of **1a** in the typical Diels–Alder manner. The principal reaction coordinates shown in Figure 2a consist of the distance r_{sS} and the angle α_{S} for the displacement of sulfur, the distances r_{sd} and $r_{\mathrm{C1'C2'}}$ and the angle α_{d} for the approaching dipolarophile, and the angle α_{CN} for the orientation of the cyano groups relative to the acetylenic axis. As r_{sd} decreases from 4 to 2.5 Å, the geometry changes in a manner consistent with the classical Diels–Alder mechanism. The sulfur atom moves up out of the plane of the thieno[3,4-*c*]thiophene system while α_{d} decreases, the acetylenic bond begins to stretch, and the cyano groups bend away from the reaction sites. An energy of activation of $E_{\mathrm{a}}^{\mathrm{c}} = 2.04$ eV (47.0 kcal mol^{-1}) was calculated. This is attributed primarily to the repulsion of the electron-charge clouds associated with the two reaction sites at a distance of $r_{\mathrm{sd}} = 2.2$ Å just prior to chemical bond formation. This large energy of activation suggested that a nonconcerted process might yield a lower energy of activation on the basis that stepwise addition should separate the interactions with C1 and C3 of the reaction site and result in lower repulsive energies for each step.

The *nonconcerted, two-step* process was analyzed by selecting $r_{\mathrm{C3C2'}}$, the distance from C3 of **1a** to C2′ of **2**, as the primary reaction coordinate. This was varied while allowing all other parameters to achieve a minimum energy configuration. The primary reaction coordinates shown in Figure 2b consist of $\alpha_{\mathrm{C2'}}$ and $\beta_{\mathrm{C2'}}$ to orient C2′, and $r_{\mathrm{C1'C2'}}$, $\alpha_{\mathrm{C1'}}$, and $\beta_{\mathrm{C1'}}$ to orient C1′. In the early stages of this reaction (shown in Figure 1), the acetylenic dipolarophile prefers to be oriented along, but not parallel to, the C3–S bond of **1a**. This is in contrast to the results obtained for a concerted mechanism in which the approaching acetylene is restrained to approach carbon atoms at positions 1 and 3 of **1a** in order to force maximum orbital overlap. These two species approach and pass through a transition state at $r_{\mathrm{C3C2'}} = 2.1$ Å which has significant dipolar character (4.05 D). As bond formation proceeds, an intermediate Ia having a dipole moment of 4.86 D is observed in which one bond is completely formed with $r_{\mathrm{C3C2'}} = 1.47$ Å, while bond formation between C1 or Ia and C1′ of **2** has not yet begun. The atoms which rearrange during formation of the second bond are separated by distances of $r_{\mathrm{C1C1'}} = 3.42$ Å and $r_{\mathrm{SC1'}} = 2.20$ Å. The sum of the van der Waals radii of two carbon atoms, and a carbon and sulfur atom, are 3.4 and 3.6 Å, respectively. The configuration about the C1′–C2′ bond orients the cyano groups with a torsional angle of 161° to give effectively trans addition to the acetylenic bond. The first activation energy of $E_{\mathrm{a1}}^{\mathrm{nc}} = 1.10$ eV (25.4 kcal mol^{-1}) showed this to be the favored initial step.

For the second step leading to the formation of the thiirane intermediate Ic from Ia, it was convenient to take $r_{\mathrm{C1C1'}}$ as the primary reaction coordinate. This was varied stepwise while allowing for the optimization of all other parameters. The path toward product formation results in another transition state having an activation energy of $E_{\mathrm{a2}}^{\mathrm{nc}} - E(\mathrm{Ia}) = 0.30$ eV (7.0 kcal mol^{-1}) with respect to the single-bonded intermediate Ia. This energy is significantly less than $E_{\mathrm{a1}}^{\mathrm{nc}} - E(\mathrm{Ia}) = 0.67$ eV (15.4 kcal mol^{-1}), which leads back to the starting materials. As bond formation proceeds, the expected cycloadduct Ib is not observed, but rather the novel thiirane Ic is formed directly with an overall energy of formation of -3.06 eV (-70.6 kcal mol^{-1}).

Formation of Ib by the concerted mechanism gave an energy of formation of -2.31 eV (-53.3 kcal mol^{-1}) relative to the reactants. A calculation, in which the orientation of the sulfur atom was selected as the reaction coordinate while all other parameters were optimized, showed that rearrangement of Ib to the thiirane Ic occurs with a negligible energy of activation. This rearrangement may be considered a thermally allowed $[\sigma^2{}_{\mathrm{a}} + \pi^2{}_{\mathrm{s}}]$ sigmatropic rearrangement in the Woodward–Hoffmann sense.[21] Both the concerted and nonconcerted paths ultimately lead to the same cycloadduct Ic which was chosen as the starting point in the search for reaction paths and a mechanism to explain the facile extrusion of elemental sulfur to yield the products illustrated in Figure 1.

Table I. Energy of $1/n$ S_n Measured Relative to the Ground State, ^3P, of Atomic Sulfur[a]

		ΔE (theory)	
$1/n$ S_n	ΔE (exptl)	chain	ring
S	0.0	0.0	
$1/2$ S_2	−2.24	−2.32	
$1/6$ S_6	−2.71	−2.75	−2.89
$1/8$ S_8	−2.76	−3.22	−3.29

[a] Experimental results obtained from ref 24 are compared to theoretical results from Figure 1.

The intermediates Id, Ie, If, and Ig are shown by these calculations to be possible intermediates along the reaction path. The transient bonding of sulfur in these intermediates should be viewed as partial bonding which changes along the reaction path in the following way. In Id, Ie, and Ig in which "three" bonds to sulfur are indicated, two are longer than either the normal S–S bond length of 1.89 Å or the C–S bond length in thiophene of 1.74 Å. In the four intermediates, the S–S bond length of the dimer Id, the bridged compound If, and the first S–S bond of the extended chain in Ie and Ig range through values of 2.13, 2.02, 1.98, and 2.05 Å, respectively. The S···C1′ bond (Figure 2) may be considered a weak bond as seen by the energy curve plotted against $r_{\mathrm{SC1'}}$ associated with Ig in which a small minimum occurs around 2.58 Å. Therefore, one may view the bridged S atoms as undergoing a change from C1–S–S–C3 in If to a weakly bonded C1–S···C1′ bridge which is the step leading toward a successive increase in the sulfur chain length.

Extrusion of Sulfur

First, the energies of the thermodynamic products are considered to assess the meaning of "extrusion of sulfur", and to establish that atomic sulfur is not the extruded form. The energies of atomic sulfur in the ^1D and ^3P states were obtained by calculating the energy of S_2 for singlet and triplet configurations at large internuclear separations. At appropriate distances, the two-center integrals vanish, and the orbitals are merely atomic orbitals of the sulfur atoms. Thus, the problem of placing half an electron on each atom in a particular MO does not arise. Convergence to these states with the computer program is assured with an initial bond-order matrix characteristic of atomic states. An examination of the filled atomic orbitals on each sulfur atom verified this separation and permitted the determination of the energy for each atomic configuration.

The extrusion of atomic sulfur from the initial cycloadducts Ib or Ic must be ruled out because of the large increase in energy. The energy of 5,6-dicyanobenzo[*c*]thiophene (**3**) and the symmetry-allowed ^1D sulfur lies 2.06 eV (47.5 kcal mol^{-1}) above the reactants, and the ^1S state of sulfur (not calculated) would yield a still higher energy. The ^3P state of sulfur and **3** lies 0.44 eV (10.1 kcal mol^{-1}) above the reactants and, in addition, it is not symmetry allowed if the expected 5,6-dicyanobenzo[*c*]thiophene is assumed to be formed directly as a singlet. Therefore, only reactions resulting in production of the more stable forms of sulfur are viable. Consequently, these species must arise by a sequence of reactions involving the novel cycloadduct Ic and other intermediates in which the number of sulfur atoms increases to that permitting ready extrusion of stable forms of sulfur. The energies for species resulting from such reactions are appropriately reported per mole of atomic sulfur. For example, one-half the energy of the dimeric species Id and $1/n$ of the energy of S_n are reported.

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(19) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301–7315.

(20) Herndon, W. C. *Chem. Rev.* **1972**, *72*, 157–179.

(21) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie Gmbh., Academic Press: Weinheim, W. Germany, 1971.

(22) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57–64.

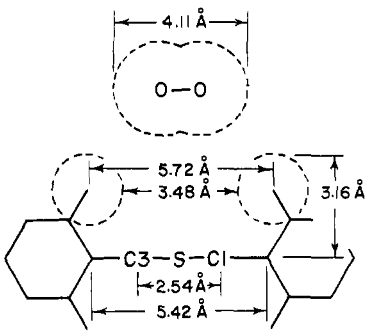

Figure 3. A view of the reaction site of 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene (**1d**) showing the steric requirements imposed by the phenyl substituents and the access afforded the oxygen molecule.

In Figure 1, the relative energies of selected linear and cyclic forms of sulfur are given for the thermodynamic products. The relative energies of sulfur in the various forms obtained experimentally[23] are in good agreement with the theoretical calculations as seen from Table I.

It was found that dimerization of the cycloadduct Ic results in a decrease in energy of 0.14 eV (3.2 kcal $\mathrm{mol^{-1}}$) to yield Id. This dimer could dissociate to give the expected product 5,6-dicyanobenzo[*c*]thiophene (**3**) and the disulfide Ie or If with an increase in energy of 0.60 eV (13.8 kcal $\mathrm{mol^{-1}}$) or 0.14 eV (3.2 kcal $\mathrm{mol^{-1}}$), respectively. These disulfide species Ie and If could undergo a dimerization reaction and subsequent dissociation to give **3** and a tetrasulfide (not shown); alternatively, they could react with the initial cycloadduct Ic with subsequent dissociation to give **3** and a trisulfide (not shown). For the myriad of anticipated reactions, it is impractical to perform all calculations. Since the energy of the compound with a linear S_8 unit Ig was similar to that of Ic, Ie, and If, it was assumed that all analogous species having extended sulfur units would have comparable energies. The ease with which molecular sulfur may be extruded from such species is demonstrated in Figure 1 for Ig by selecting the bond length $r_{\mathrm{SC1'}}$ as the reaction coordinate which is increased as all other parameters are allowed to achieve a minimum energy configuration. This results in a small activation energy as the products **3** and linear S_8 are formed.

Extrusion of sulfur occurs because of the existence of forms more stable than diatomic sulfur. It appears that this fact distinguishes sulfur from the more stable analogous oxygen- and nitrogen-bridged heterocycles.

Steric Constraints, Rotational Barriers, and Chemical Reactivity

To examine the effect of steric interference, **1d** and **1e** were studied theoretically. A view along the S–S axis with the phenyl substituents oriented perpendicular to the thieno[3,4-*c*]thiophene nucleus is shown in Figure 3. The ortho hydrogen atoms of the phenyl substituents have an interatomic separation of 5.72 Å. With their van der Waals radii, they extend 3.16 Å above the ring system and provide a 3.48-Å opening for approach to the reaction site. In this conformation they effectively shield the reaction sites whose π orbitals extend 1.7 Å above the ring system. The oxygen molecule requires only 4.11 Å (r_{OO} = 1.21 Å, van der Waals radius = 1.45 Å) to gain access to the reaction site.

In the proposed two-step mechanism, dipolarophiles can only gain access to the reaction site if one of the phenyl substituents is nearly coplanar with the thieno[3,4-*c*]thiophene ring system. A lower limit to the angle of rotation, at which the ortho hydrogen atoms of the phenyl substituents are the same height as the π system, thereby exposing the reaction site, is calculated to be 31.3°. In a concerted reaction, both phenyl substituents at positions 1 and 3, or 4 and 6, must be nearly planar. The probability of such an occurrence is approximately the square of that for one phenyl group because both phenyl substituents must simultaneously be favorably oriented for a concerted reaction. It is anticipated that the probability is much larger for a nonconcerted mechanism because formation of the first chemical bond influences the orientation of the other phenyl group on the second site by the proximity of the dienophile and the subsequent steric repulsion which will tend to force the phenyl group into more favorable conformations. Therefore, both the steric constraints and the observed reactivity favor a stepwise mechanism. To determine the effect of the rotation of the phenyl substituents on the rate of reaction, the energy barrier of rotation of the phenyl substituents was evaluated theoretically. This was accomplished by studying the interaction of the *peri*-phenyl substituents of 1,6-diphenylthieno[3,4-*c*]thiophene (**1e**).

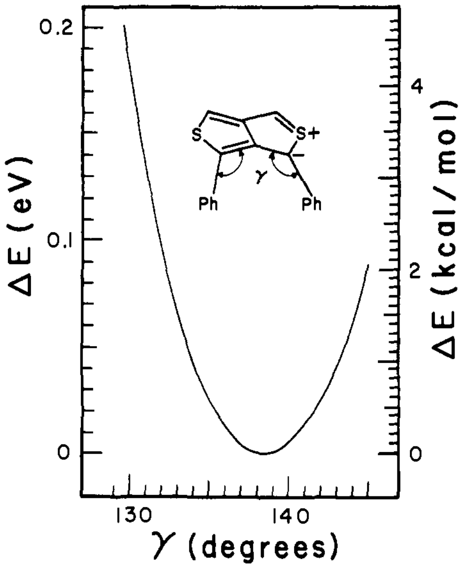

Figure 4. Plot of energy vs. splaying angle γ in 1,6-diphenylthieno[3,4-*c*]thiophene (**1e**) with the phenyl substituents perpendicular to the parent ring system.

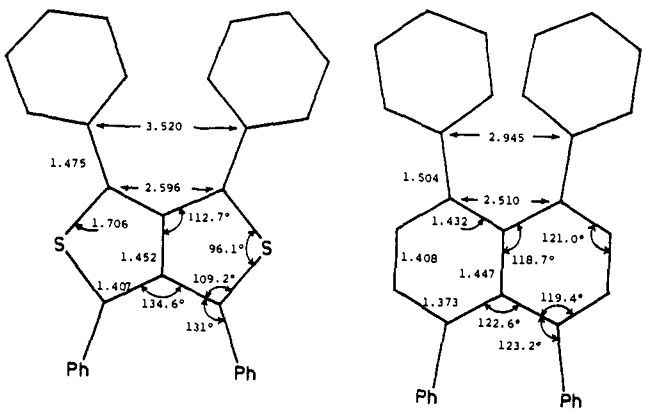

Figure 5. X-ray crystal structures of 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene (**1d**) and 1,4,5,8-tetraphenylnaphthalene (**4a**).

First, with both phenyl substituents perpendicular to the ring system, the optimum splaying angle, γ, was determined to be 138.2° as shown in the plot of energy vs. splaying angle in Figure 4. This agrees well with the experimental value[24,25] of 131° in Figure 5. With this value for γ, the phenyl substituents were rotated and the relative energies determined. Figure 6 shows the results for two conrotatory and two disrotatory modes of rotations. Rotation of one phenyl group while maintaining the other at 90°

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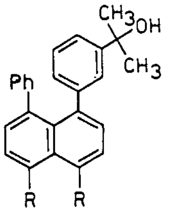
[23] Kelley, K. K. "Contributions to the Data on Theoretical Metallurgy". VII. The Thermodynamic Properties of Sulfur; Its Inorganic Compounds"; *U.S. Bur. Mines Bull.* **1937**, *406*, Table 78.

[24] The value of the internal splaying angles for the phenyl substituents of 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene (**1d**) has not been previously reported but was calculated from the X-ray crystallographic data.[25]

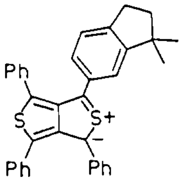
[25] Glick, M. D.; Cook, R. E. *Acta Crystallogr., Sect. B* **1972**, *28*, 1336–1339.

provides a rotational barrier of 0.29 eV (6.7 kcal mol^{-1}). This is considerably lower than that determined for the structurally similar naphthalene derivatives **4** and **5** of 0.71 eV (16.4 kcal mol^{-1})[26] and 0.65 eV (14.9 kcal mol^{-1}),[27] respectively. The discrepancy can, to a great extent, be explained by the greater steric interaction of the phenyl substituents in **4** and **5** which is evident from the nonplanarity of the naphthalene nucleus,[28,29] whereas, the thieno[3,4-*c*]thiophene system of **1d** is planar. This is attributed to the greater internuclear separation of the atoms bearing the phenyl substituents and the larger splaying angle of **1d** compared to tetraphenylnaphthalene as seen in Figure 6. Rotations of the phenyl groups for which $\omega_1 = \omega_2$ and $\omega_1 = 180° - \omega_2$ exhibit large steric repulsions as the two phenyl substituents approach a planar configuration. For the case where $\omega_1 = 90° + \omega_2$, a barrier of approximately 0.74 eV (17 kcal mol^{-1}) is obtained at $\omega_1 = 135°$ and $\omega_2 = 45°$. In general, as ω_1 deviates from 90°, the barrier to rotation about ω_2 increases. Therefore, the barrier to internal rotation is a function of both ω_1 and ω_2, but the effective rotational barrier should nevertheless be about 0.29 eV (6.7 kcal mol^{-1}). These theoretical calculations prompted a study of the rotational barrier of the tetraphenyl derivative **1d** which was found to lie between 5 and 9.2 kcal mol^{-1}, in good agreement with the 1,3-diphenyl derivative.[30] As a chemical reaction at positions 1 and 3 of **1** is of interest, it is assumed that the phenyl groups of positions 1 and 3 are free to rotate subject to the phenyl groups in positions 4 and 6 which are fixed at 90°.

The free energy of rotation for *peri*-phenyl substituents of phenylnaphthalenes has been shown[27] to be 0.71 eV (16.4 kcal mol^{-1}) by dynamic NMR methods, the carbinol **4** being used as a model. In a similar investigation, the system **5** containing four phenyl substituents was found[26] to have an energy of rotation of the *peri*-phenyl substituents of 0.65 eV (14.9 kcal mol^{-1}).



4, R = H
5, R = C_6H_5



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These values are significantly greater than those predicted on the basis of the previously described theoretical model for 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene (**1d**). In part, the discrepancy was attributed to the inability of the model system to evaluate the contribution of concomitant rotation of both *peri*-phenyl substituents on the rotational barrier. The experimental value was therefore expected to be greater than the calculated value of 0.29 eV (6.7 kcal mol^{-1}) though not as great as in the case of **4** and **5**. This prompted the experimental study of the rotational activation parameters of **6** which possesses phenyl substituents having geometrical relationships similar to those of the *peri*-phenylnaphthalenes. A different phenyl equivalent possessing diasteriotopic substituents in the meta position is necessary for this investigation because of the severity of the reaction conditions employed in synthesizing thieno[3,4-*c*]thiophenes. 1-(1,1-Dimethyl-6-indanyl)-3,4,6-triphenylthieno[3,4-*c*]thiophene (**6**) was synthesized by the reaction sequence shown in Scheme I.

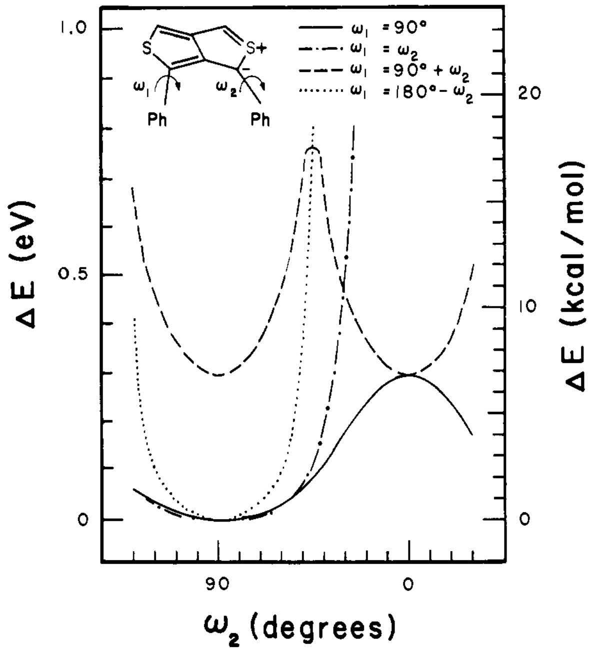
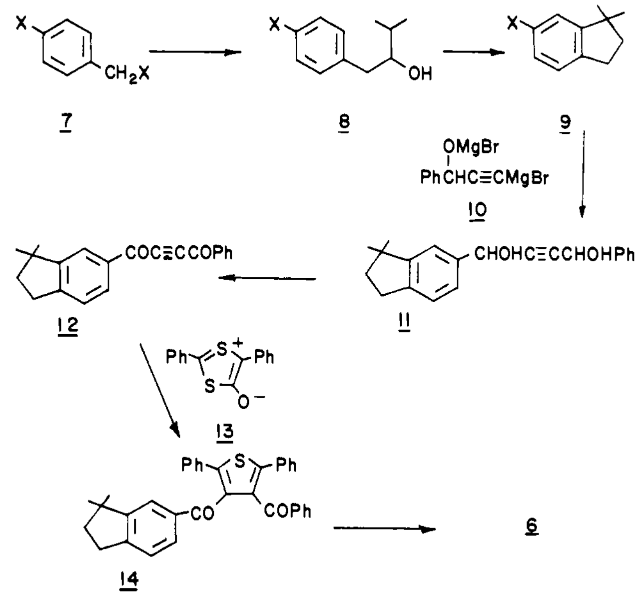


Figure 6. Plots of the relative energy vs. the rotational angle of the phenyl substituents of 1,6-diphenylthieno[3,4-*c*]thiophene (**1f**) with a constant splaying angle of 138.2° for two conrotatory ($\omega_1 = \omega_2$ and $\omega_1 = 90° + \omega_2$) and two disrotatory ($\omega_1 = 90° - \omega_2$ and $\omega_1 = 180° - \omega_2$) types of rotation.

Scheme I. Synthesis of 1-(1,1-Dimethyl-6-indanyl)-3,4,6-triphenylthieno[3,4-*c*]thiophene (6)



Formation of the Grignard reagent from 4-chlorobenzyl chloride (**7**, X = Cl) or 4-bromobenzyl bromide (**7**, X = Br) and reaction with 2-methylpropanal (isobutyraldehyde) afforded the corresponding 1-(4-halophenyl)-3-methyl-2-butanols **8** (X = Cl, Br). These underwent facile cyclodehydration in 90% sulfuric acid to give the 6-halo-1,1-dimethylindans **9** (X = Cl, Br) in 37 and 44% overall yield, respectively.

6-Chloro-1,1-dimethylindan (**9**, X = Cl) proved to be unreactive and could not be converted into the desired aldehyde. The Grignard reagent could not be formed in refluxing ether or THF even when an entrainment reaction using 1,2-dibromoethane was utilized. Reaction with lithium or finely divided sodium sand in refluxing THF also proved ineffective, affording only unreacted starting material.

In contrast, 6-bromo-1,1-dimethylindan (**9**, X = Br) reacted with magnesium in ether at room temperature to give the Grignard reagent. Reaction with freshly distilled triethyl orthoformate in refluxing ether overnight followed by acid hydrolysis gave the

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desired aldehyde **9** (X = CHO) in 14% yield along with 1,1-dimethylindan (66%). Use of *N,N*-dimethylformamide increased the yield of 1,1-dimethylindan-6-carboxaldehyde to 43% while 1,1-dimethylindan was obtained in 29% yield.

Reaction of the aldehyde **9** (X = CHO) with the Grignard complex **10** derived from 1-phenyl-2-propyn-1-ol gave the diol **11** (47%) which was oxidized with Jones' reagent to the corresponding dione **12** (81%). Treatment of the dione **12** with *anhydro*-4-hydroxy-2,5-diphenyl-1,3-dithiolium hydroxide (**13**) gave the corresponding thiophene **14** (90%). Phosphorus pentasulfide in refluxing pyridine (18 h) and **14** resulted in the formation of 1-(1,1-dimethyl-6-indanyl)-3,4,6-triphenylthieno[3,4-*c*]thiophene (**6**) as purple microprisms, mp 90–95 °C.

Sublimation of **6** at 160 °C (10^{-6} mm) was used to prepare the sample utilized in the NMR experiment. At 30 °C the methyl groups of the indanyl moiety were a sharp singlet at δ 1.08, while the indanyl C2 and C3 methylene protons formed a pair of triplets at δ 1.84 and 2.81, respectively (J = 7.0 Hz). The aromatic protons gave two distinct double doublets at δ 7.69 (J = 8.25 and 1.6 Hz) and 7.50 (J = 7.5 and 2.4 Hz), each equivalent to one proton. The 16 remaining aromatic protons formed a poorly resolved multiplet at δ 6.90–7.42. Signal broadening of the ^{1}H NMR spectrum was only observed below −90 °C while the sample solidified at −100 °C, preventing the acquisition of sufficient data to perform an exact analysis.

These results, however, do define an upper limit for the energy of activation for the rotation of the phenyl substituents, assuming the expected shift difference for the two exchange sites to be ca. 3.5 Hz, that observed in the case of the *peri*-phenylnaphthalene **4**, and, assuming that the coalescence temperature is below 173 K (−100 °C), an upper limit for the enthalpy of activation is 0.40 eV (9.2 kcal mol^{-1}). It should be noted that a change in the shift difference has little effect on the calculated coalescence temperature, and this value is consistent with the rotational activation energy determined theoretically.

Discussion

Ab initio calculations using a STO-3G basis set and 3 × 3 configuration interaction (CI) are known to favor a symmetrical transition state whereas MINDO/3 favors an unsymmetrical biradical transition state for the cycloaddition of ethylene with butadiene, and fulminic acid with acetylene.[18] This was attributed to the basic differences between the semiempirical and ab initio techniques. It has been suggested that the semiempirical methods, such as MINDO/3, are likely to underestimate the stability, i.e., overestimate the energy, of a symmetrical transition state relative to an unsymmetrical one owing to the neglect of differential overlap which excludes the symmetry-dependent repulsive forces. Dewar has pointed out, however, that such errors should, to a great extent, be compensated in MINDO/3 by the parameterization designed to reproduce experimental results.[31] Though such comparisons are helpful in understanding the difficulties that may be encountered, one must ultimately rely on the results of a series of calculations employing a consistent technique. Therefore, in an investigation of a reaction surface, it is appropriate to concentrate on the differences in energy of the various reaction paths which, in this case, favor a two-step dipolar mechanism.

Dewar, using MINDO/3 and including CI, found that a two-step biradical mechanism was preferred in the cycloaddition reaction of ethylene with butadiene.[32] The calculated energy of activation of 1.22 eV (28.2 kcal mol^{-1}) was in excellent agreement with the experimental value of 1.19 eV (27.5 kcal mol^{-1}).[33] This result was supported by a subsequent study of the retro-Diels–Alder reaction of cyclohexene.[31] The biradical mechanism was pursued on the basis of the "extreme asymmetry of the transition state" which was interpreted to imply a "high degree of biradical character", but asymmetry can also imply dipolar character. These results, therefore, do not necessarily contradict those of the present study, and they agree in so far as a two-step mechanism is favored over the concerted one.

In the present study, inspection of the molecular orbitals of each of the species whose energy was calculated shows a large HOMO/LUMO energy difference which precludes the possibility of a biradical. Configuration interaction would result in an improvement in the energy of such biradicals and has been found to be useful, but it has also been pointed out that in semiempirical treatments this is incorrect in principle.[34] The possibility of a biradical being involved in our model reaction was not pursued on the basis of the acceptability of the observed energy of activation for the proposed mechanism and the absence of nearly degenerate HOMO and LUMO. The energy of activation for our model reaction has not been determined experimentally, but the assumed high rate implies an energy of activation ≤20 kcal mol^{-1} based on the Arrhenius equation assuming a reaction at 300 K with a half-life ≤10 min and an Arrhenius frequency factor of 10^6. The calculated value of 1.14 eV (26.4 kcal mol^{-1}) is in reasonable agreement with these observations and is comparable to the calculated and experimentally determined value for the cycloaddition reaction of butadiene with ethylene previously discussed.

Steric restraints, especially with dimethyl fumarate and dimethyl maleate, have recently been shown to be of prime importance in determining the configuration at the carbons of the cycloadducts in the *anhydro*-4-hydroxy-2,3,5-triphenyl-1,3-thiazolium hydroxide system,[35] a mesoionic ring system containing the thiocarbonyl ylide dipole also present in **1**. The lack of reactivity of the structurally related heteropentalene 2-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole toward dimethyl maleate and dimethyl fumarate has also been interpreted as being the result of steric interference.[7]

There are obvious advantages of a two-step mechanism vs. a concerted mechanism in reactions involving steric control. The consecutive formation of bonds allows for drastic geometrical changes, that is, changes in hybridization of the two reacting species during the course of the cycloaddition reaction. This allows the mechanism to accommodate bulkier substituents and to minimize their effect on the rate. Even so, it can still be the controlling factor as proposed for this case.

Extending the model reaction to the case of **1b**, a concerted mechanism requires both phenyl substituents at C1 and C3 of **1b** to be in a favorable orientation for bond formation. Assuming a maximum allowable angle of rotation to be 32°, the energy of activation for the reaction would increase by 0.43 eV (9.9 kcal mol^{-1}), thereby decreasing the rate by a factor of 6.0×10^{-10} at 300 K and 3.9×10^{-6} at 400 K.

In contrast, the proposed two-step dipolar mechanism would only require that the phenyl substituent at the carbon involved in the initial bond formation have a favorable orientation, which would increase the energy of activation by 0.22 eV (5.1 kcal mol^{-1}) and decrease the rate by only 1.9×10^{-4} at 300 K and 1.6×10^{-3} at 400 K. Such dramatic effects are consistent with the observed differences in the reactivity of **1b** with oxygen and acetylenic dipolarophiles. It is also consistent with the inability to isolate **1d** and **1e** vs. **1b**. In addition, this suggests that other derivatives of **1** containing bulky substituents in the 1, 3, 4, and 6 positions may be isolable.

It is known that 1-(4-methoxyphenyl)-3,4,6-triphenylthieno[3,4-*c*]thiophene (**1f**) preferentially adds dipolarophiles across C1 and C3.[8] The steric effects at the two potential reactive sites are essentially equal and cannot explain this selectivity. The low-energy barrier of rotation calculated for phenyl substituents suggests that they should be undergoing rapid rotation in solution. This allows for the interaction of the MO's of the phenyl substituents with those of the parent ring system **1**, as evidenced by the electronic absorption spectrum of **1b**. Therefore, the 4-

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methoxyphenyl substituent can exert control over the course of the reaction as would be predicted by MO theory and in accord with the proposed dipolar mechanism. This would also be the expected result based on a concerted or biradical mechanism.

A most interesting result of the model reaction surface is the proposed mechanism for thermal extrusion of sulfur. Such reactions have proven to be important synthetic processes. The photochemical and related high-temperature flash-thermolytic extrusion of sulfur occurs by a radical mechanism and the thermal extrusion of sulfur in the presence of trivalent phosphorus reagents most likely involves the formation of a zwitterionic intermediate which subsequently extrudes trisubstituted phosphorus sulfide. In contrast, no mechanism has previously been proposed for the unassisted thermal extrusion of sulfur.

The thermal extrusion of atomic sulfur at moderate temperatures is not a viable process because of the prohibitive energy of activation. The results of this study indicate that, in those cases where such reactions are observed, it is the result of a sequence of reactions resulting in the formation of transient intermediates possessing multiple sulfur chains or bridges. These may subsequently be readily extruded to give more stable forms of elemental sulfur. The driving force for this reaction is the formation of the more stable products. The proposed mechanism suggests that the ease with which sulfur is extruded will be susceptible to substituent effects since the first step in the sequence involves dimerization of a mono-sulfur-containing intermediate.

The apparent enhanced stability of a number of the proposed intermediates in Figure 1 relative to the expected products is attributed to the overestimation of the stability of small ring compounds. This is not significant in terms of the overall trend.

Experimental Section[36]

1-(4-Chlorophenyl)-3-methyl-2-butanol (8, X = Cl). 4-Chlorobenzyl chloride (**7**, X = Cl; 161.0 g, 1.00 mol) in ether (125 mL) was added to a stirred suspension of magnesium turnings (25.0 g, 1.02 mol) in ether (200 mL) at such a rate that a gentle reflux was maintained. The reaction mixture was refluxed for an additional 30 min and cooled in an ice bath; 2-methylpropionaldehyde (100.0 g, 1.39 mol) in ether (100 mL) was then added over a period of 5 h. After stirring overnight at room temperature, the reaction mixture was cooled in ice while ice (150 g) was added, followed by sufficient concentrated aqueous HCl to give a clear homogeneous aqueous phase which was separated and extracted with ether (2 × 100 mL). The combined organic extracts were washed successively with three portions of water and saturated salt solution, then dried (anhydrous Na_2SO_4), and evaporated. Distillation afforded 1-(4-chlorophenyl)-3-methyl-2-butanol (**8**, X = Cl) as a colorless oil which formed colorless waxy needles on standing: 151.0 g (78%), bp 86–92 °C (0.10 mm), mp 30–33 °C; IR (thin film) 3400 (OH), 2960, 2940, 2880 (CH), 810 (Ph) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88–7.31 (m, 4, aromatic), 3.40 (dt, 1, $J = J' = 4.0$ Hz, CH), 2.65 (d, 1, $J = 4.0$ Hz, CH_2), 1.77 (s, 1, OH), 1.27–1.77 (m, 1, CH), 0.93 (d, 6, $J = 7.0$ Hz, 2 CH_3); *m/e* (% rel intensity) M^+ 198 (5.5), 125 (100).

Anal. Calcd for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61. Found: C, 66.52; H, 7.57.

6-Chloro-1,1-dimethylindan (9, X = Cl). 1-(4-Chlorophenyl)-3-methyl-2-butanol (**8**, X = Cl; 99.4 g, 0.50 mol) was added in small portions to aqueous sulfuric acid (90%, 250 mL) at 10 °C over a period of 1 h; the mixture was then stirred at room temperature for 2 h and poured onto ice (1 kg). The aqueous layer was separated and extracted with ether (3 × 200 mL). The combined organic extracts were washed successively with three portions of water and saturated salt solution, then dried (anhydrous Na_2SO_4), and evaporated. Distillation of the residual yellow oil afforded 6-chloro-1,1-dimethylindan (**9**, X = Cl) as a colorless sweet-smelling oil: 42.8 g (47%), bp 56 °C (0.02 mm); IR (thin film) 2955, 2860 (CH), 877, 860, 815 (Ph) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0 (bs, 3, aromatic), 2.79 (t, 2, $J = 7.0$ Hz, CH_2), 1.87 (t, 2, $J = 7.0$ Hz, CH_2), 1.20 (s, 6, 2 CH_3); *m/e* (% rel intensity) M^+ 180 (5.5), 28 (100).

Anal. Calcd for $C_{11}H_{13}Cl$: C, 73.12; H, 7.51. Found: C, 73.15; H, 7.32.

1-(4-Bromophenyl)-3-methyl-2-butanol (8, X = Br). 4-Bromobenzyl bromide (250.0 g, 1.00 mol) in ether (1.5 L), in a 3-L, three-neck round-bottomed flask that was fitted with an Erlenmeyer flask containing magnesium turnings (25.0 g, 1.02 mol) using a piece of Gooch tubing, was cooled to 0 °C under anhydrous conditions using a dry ice/acetone bath. A few magnesium turnings were added and, after they were consumed, the reaction mixture was cooled to −40 °C. The remaining magnesium turnings were added in one portion; the temperature was maintained at −40 to −30 °C until the reaction was completed (2 h), and then allowed to warm to 0 °C. 2-Methylpropanal (95.0 g, 1.3 mol) in ether (400 mL) was added over a period of 4 h at 0 °C; the mixture was stirred at room temperature overnight. The reaction mixture was cooled in an ice bath; ice (200 g) was added followed by sufficient concentrated aqueous HCl to give a clear homogenous aqueous phase, which was separated and extracted with ether (2 × 200 mL). The combined organic extracts were washed successively with water and saturated salt solution, then dried (anhydrous Na_2SO_4), and evaporated. Distillation afforded 1-(4-bromophenyl)-3-methyl-2-butanol (**8**, X = Br) as a colorless, sweet-smelling oil which readily crystallized as colorless waxy needles: 145.0 g (60%), bp 94–95 °C (0.05 mm), mp 43–45 °C; IR (thin film) 3300 (OH), 2950, 2860 (CH), 542 (PhBr) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27 (d, 2, $J = 8.0$ Hz, aromatic), 6.98 (d, 2, $J = 8.0$ Hz, aromatic), 3.45 (dt, 1, $J = 4.0$ Hz, $J' = 4.0$ Hz, CH), 2.64 (d, 2, $J = 4.0$ Hz, CH_2), 1.70 (s, 1, OH), 1.38–1.87 (m, 1, CH), 0.96 (d, 6, $J = 6.0$ Hz, 2 CH_3); *m/e* (% rel intensity) M^+ 244 (2), 242 (2), 43 (100).

Anal. Calcd for $C_{11}H_{15}BrO$: C, 54.33; H, 6.22. Found: C, 54.59; H, 6.19.

6-Bromo-1,1-dimethylindan (9, X = Br). Finely divided 1-(4-bromophenyl)-3-methyl-2-butanol (24.3 g, 0.10 mol) was added to sulfuric acid (90%, 85 mL) over a period of 15 min with vigorous stirring; the mixture was then warmed to 50 °C for 10 min, allowed to cool to room temperature, and poured onto ice (200 g). The aqueous layer was separated and extracted with ether (2 × 100 mL). The combined organic extracts were washed successively with water and aqueous potassium carbonate (10%), then dried (anhydrous Na_2SO_4), and evaporated. Distillation afforded 6-bromo-1,1-dimethylindan (**9**, X = Br) as a colorless sweet-smelling oil: 16.4 g (73%), bp 62–63 °C (0.06 mm) (lit.[37] bp 65–68 °C (0.20 mm)); IR (thin film) 2490, 2850 (CH), 642 (ArBr) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.73–7.23 (m, 3, aromatic), 2.73 (t, 2, $J = 7.0$ Hz, CH_2), 1.82 (t, 2, $J = 7.0$ Hz, CH_2), 1.15 (s, 6, 2 CH_3); *m/e* (% rel intensity) M^+ 226 (31), 224 (32), 130 (100).

Anal. Calcd for $C_{11}H_{13}Br$: C, 58.68; H, 5.82. Found: C, 58.92; H, 5.98.

1,1-Dimethyl-6-indancarboxaldehyde (9, X = CHO). 6-Bromo-1,1-dimethylindan (22.3 g, 0.10 mol) in ether (100 mL) was added to a stirred suspension of magnesium turnings (2.50 g, 0.10 mol) in ether (50 mL) under anhydrous conditions at such a rate that a gentle reflux was maintained. The turbid green reaction mixture was refluxed for 2 h and cooled to −30 °C using a dry ice/acetone bath; dry DMF (7.40 g, 0.10 mol) in ether (50 mL) was added as quickly as possible. An intractable mass formed rapidly leaving a yellow solution which was allowed to warm to room temperature overnight. While cooling in ice, ice (100 g) was added followed by sufficient concentrated aqueous HCl to give a clear homogenous aqueous phase which was separated and extracted with ether (2 × 50 mL). The combined organic extracts were washed successively with two portions of water, aqueous sodium bicarbonate (10%), and saturated salt solution, then dried (anhydrous Na_2SO_4) and evaporated; the residual oil was fractionally distilled. 1,1-Dimethylindan (**9**, X = H) distilled as a colorless oil: 4.30 g (29%), bp 68–75 °C (14 mm) (lit.[38] bp 191 °C). 1,1-Dimethyl-6-indancarboxaldehyde (**9**, X = CHO) distilled as a colorless, sweet-smelling oil: 7.49 g (43%), bp 120–125 °C (14 mm); IR (thin film) 2900, 2845, 2730 (CH), 1700 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.50 (s, 1, CHO), 6.64–7.33 (m, 3, aromatic), 2.43 (t, 2, $J = 7.0$ Hz, CH_2), 1.28 (t, 2, $J = 7.0$ Hz, CH_2), 0.80 (s, 6, 2 CH_3); *m/e* (% rel intensity) M^+ 174 (35), 159 (100).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.52; H, 8.84.

1-(1,1-Dimethyl-6-indanyl)-4-phenyl-2-butyne-1,4-diol (11). 1-Phenyl-2-propyn-1-ol (13.2 g, 0.10 mol) in benzene (60 mL) was added under nitrogen over a period of 30 min to a freshly prepared, dark-gray

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[36] Spectral characterizations were performed on the following instruments: infrared spectra, Perkin-Elmer Model 337 spectrophotometer; ^1H NMR spectra, Varian T-60, Varian HA-100, and Bruker 270, using $(CH_3)_4Si$ as an internal standard; ^{13}C NMR, Bruker WP-60 and Bruker 270, using $(CH_3)_4Si$ as an internal standard; mass spectra, Hitachi Perkin-Elmer RMU-6E mass spectrometer utilizing a direct insertion probe for solid samples or a variable-leak gas/liquid inlet and operated with a source temperature of 175 °C. Melting points were determined using a Thomas Hoover capillary melting point apparatus for samples melting below 220 °C and a Mel-Temp capillary melting point apparatus for those melting above 220 °C. Evaporations were carried out under reduced pressure using a Buchi Rotovap apparatus. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Instranal Laboratories, Inc., Rensselaer, N.Y.

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ethylmagnesium bromide solution (0.21 mol) in ether (100 mL) with the evolution of ethane. A jade green oily precipitate formed leaving a turbid yellow solution. After refluxing for 1 h, the reaction mixture was cooled to room temperature and 1,1-dimethyl-6-indancarboxaldehyde (0.10 mol) in ether (50 mL) was added over a period of 30 min; the solution was then refluxed overnight. The reaction mixture was cooled in ice, and ice (50 g) was added followed by sufficient concentrated aqueous HCl to dissolve the precipitated magnesium salts and the unreacted magnesium. The aqueous layer was separated and extracted twice with ether. The combined organic phases were washed successively with water and saturated salt solution, then dried (anhydrous Na_2SO_4), and evaporated. The desired butynediol which precipitated from the residual oil on standing was collected and crystallized as colorless prisms (47%) from $CHCl_3$/petroleum ether (60–80 °C): mp 105–106 °C; IR (KBr) 3210 (OH), 3080, 3030, 2950, 2860 (CH), 760, 700 (Ph) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20–7.70 (m, 8, aromatic), 5.57 (bs, 2, 2 CH), 2.73 (t, 2, J = 7.0 Hz, indanyl CH_2), 2.21 (bs, 2, 2 OH), 1.90 (t, 2, J = 7.0 Hz, indanyl CH_2), 1.27 (s, 6, 2 CH_3); ^{13}C NMR ($CDCl_3$) ppm 153.21, 143.40, 140.41, 138.68, 128.64, 128.43, 126.62, 124.87, 124.66, 120.39, 86.85, 86.16, 65.00, 64.74, 44.00, 41.60, 29.84, 28.59; *m/e* (% rel intensity) M^+ 306 (100).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.25; H, 7.24. Found: C, 82.25; H, 7.29.

1-(1,1-Dimethyl-6-indanyl)-4-phenyl-2-butyne-1,4-dione (12). The diol (10 mmol) in acetone (100 mL) was treated with an excess of Jone's reagent (1.0 g of CrO_3 in 2.7 mL of H_2O and 1.0 mL of concentrated H_2SO_4) over 15 min while cooling in ice, resulting in a red-brown solution and an intractable green precipitate. The reaction mixture was stirred for an additional hour at room temperature; then sufficient 2-propanol was added to consume excess oxidizing agent, a green solution being obtained. The reaction mixture was filtered and concentrated to 20 mL; water (30 mL) was added and the mixture was extracted with ether (3 × 20 mL). The combined organic extracts were washed successively with several portions of water, aqueous sodium bicarbonate (10%), and saturated salt solution, then dried (anhydrous Na_2SO_4), and evaporated to give 1-(1,1-dimethyl-6-indanyl)-4-phenyl-2-butyne-1,4-dione (**12**) as fluffy, glistening cream-colored plates (81%) from chloroform/methanol: mp 72–73 °C; IR (KBr) 3060, 2950, 2930, 2850 (CH), 1750 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–8.37 (m, 8, aromatic), 2.92 (t, 2, J = 7.0 Hz, indanyl CH_2), 1.92 (t, 2, J = 7.0 Hz, indanyl CH_2), 1.21 (s, 6, 2 CH_3); ^{13}C NMR ($CDCl_3$) ppm 176.62, 176.35, 153.89, 151.74, 136.04, 135.04, 134.96, 129.76, 129.38, 128.90, 124.96, 122.83, 86.48, 85.38, 43.93, 41.24, 30.53, 28.50; *m/e* (% rel intensity) M^+ 302 (20), 287 (100).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.17; H, 6.14.

3-Benzoyl-2,5-diphenyl-4-(1,1-dimethyl-6-indanoyl)thiophene (14). 4-(1,1-Dimethyl-1-indanyl)-1-phenyl-2-butyne-1,4-dione (10 mmol) and *anhydro*-4-hydroxy-2,5-diphenyl-1,3-dithiolium hydroxide[39] (**13**, 2.70 g, 10 mmol) in refluxing toluene (50 mL) for 10 days afforded a red oil which was taken up in chloroform and treated with several portions of charcoal until a yellow solution was obtained. Evaporation of the solvent and treatment of the resulting oil with methanol afforded pale yellow prisms (90%); mp 156–156.5 °C; IR (KBr) 3050, 3010, 2950, 2850 (CH), 1660, 1630 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83–7.92 (m, 18, aromatic), 2.80 (t, 2, J = 7.0 Hz, indanyl CH_2), 1.83 (t, 2, J = 7.0 Hz, indanyl CH_2), 1.09 (s, 6, 2 CH_3); ^{13}C NMR ($CDCl_3$) ppm 192.88, 192.71, 152.55, 148.89, 144.23, 144.16, 139.10, 138.76, 137.33, 136.04, 132.85, 132.46, 132.37, 129.68, 128.97, 128.94, 128.78, 128.57, 128.55, 128.54, 128.41, 128.04, 124.13, 123.37, 43.66, 41.23, 30.18, 28.38; *m/e* (% rel intensity) M^+ 512 (100).

Anal. Calcd for $C_{35}H_{28}O_2S$: C, 82.00; H, 5.50. Found: C, 81.89; H, 5.55.

1-(1,1-Dimethyl-6-indanyl)-3,4,6-triphenylthieno[3,4-*c*]thiophene (6). 3-Benzoyl-4-(1,1-dimethyl-6-indanoyl)-2,5-diphenylthiophene (**14**, 1.03 g, 2.00 mmol) and phosphorus pentasulfide (0.51 g, 2.3 mmol) were refluxed in pyridine (50 mL) for 18 h under nitrogen. The warm solution was poured onto ice (150 g) and crystallization was induced by addition of acetic acid (1 mL) and scratching the walls of the flask. The product was collected using a sintered glass funnel, washed with fresh water, and then dried over phosphorus pentoxide under reduced pressure to give purple microprisms: 1.02 g (99%), mp 90–95 °C. Recrystallization from acetic anhydride under a blanket of nitrogen gave fine, glistening, purple prisms consisting of one component by TLC (silica/chloroform), mp 90–95 °C, but neither recrystallization nor fractional sublimation afforded an analytically pure sample; ^1H NMR (CD_2Cl_2) δ 7.67–7.73 (m, 1, aromatic), 7.50 (dd, 1, J = 7.54 Hz, J' = 2.4 Hz, aromatic), 7.29–7.42 (m, 6, aromatic), 6.90–7.29 (m, 9, aromatic), 2.81 (t, 2, J = 7.0 Hz, indanyl CH_2), 1.84 (t, 2, J = 7.0 Hz, indanyl CH_3), 1.08 (s, 6, 2 CH_3); *m/e* (% rel intensity) M^+ 512 (100).

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Registry No. **1a**, 24976-21-4; **1d**, 23386-93-8; **1e**, 84648-09-9; **2**, 1071-98-3; **6**, 84648-10-2; **7** (X = Cl), 104-83-6; **7** (X = Br), 589-15-1; **8** (X = Cl), 42024-40-8; **8** (X = Br), 84648-11-3; **9** (X = Cl), 84648-12-4; **9** (X = Br), 67159-88-0; **9** (X = CHO), 84648-13-5; **10**, 84648-14-6; **11**, 84680-79-5; **12**, 84680-80-8; **13**, 20850-89-9; **14**, 84680-81-9; 2-methylpropanol, 78-84-2; triethyl orthoformate, 122-51-0; 1-phenyl-2-propyn-1-ol, 4187-87-5.

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[39] Gotthardt, H.; Weisshuhn, M. C.; Christl, B. *Chem. Ber.* **1976**, *109*, 740–760.