

The Photochemical Reaction of (*E,E*)-Dibenzylidenesuccinic Thioanhydride: A Spectroscopic and Structural Study

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Received 7 December 1989.

ABSTRACT

The first photochromic thioanhydride, (*E,E*)-2,3-dibenzylidenesuccinic thioanhydride (**1b**), was synthesized. Irradiation of (**1b**) in benzene, dichloromethane, or chloroform gives isomerization and cyclization products similar to those obtained for the anhydride analogue (**1a**). The crystal structure of (**1b**) was determined (X-rays) and compared to the structures of the anhydride (**1a**) and N-phenylimide (**1c**). ¹H and ¹³C NMR spectra were recorded, and the electron charge densities of the carbon atoms were calculated with AM1. These results are discussed and compared with those for the compounds **1a**–**1c**. The thioanhydride (**1b**) ring is much more twisted than either the anhydride (**1a**) or the imide (**1c**) rings. The linear relationship between the ¹³C NMR chemical shifts and the electron charge density on the given atom has been investigated. The C(carbonyl) and C(α) carbon atoms of **1b** were found to be greatly deshielded relative to the corresponding atoms in **1a** and **1b**. The increase in sensitivity toward cyclization of the thioanhydride (**1b**) is attributed to the marked change in the charge distribution.

Crystal data. Thioanhydride (**1b**): space group *P2₁/c* with *a* = 12.956(3) Å, *b* = 14.843(6) Å, *c* = 7.512(6) Å, β = 98.05(2)°, *R*_w = 0.085 and *R* = 0.089.

INTRODUCTION

Photochromism is currently a topic of active research. Objectives for future research include mod-

ifying already known systems, so as to obtain improved properties for specific applications. Photochromic substances of the fulgide type have until now been limited to succinic anhydride- [1] and *N*-substituted succinimide [2] derivatives with only the substituents on the 1,3-butadiene system being changed to obtain certain properties. It was reported previously that the compounds (*E,E*)-dibenzylidenesuccinic anhydride [3] and (*E,E*)-dibenzylidene-*N*-phenylsuccinimide [4] cyclize by a conrotatory mode to give red 1,8a-1-phenyl-dihydronaphthalene derivatives (1,8a DHNs) on irradiation at 366 nm, in solution or in the solid state, and that the 1,8a DHNs undergo the reverse reaction by a disrotatory mode on exposure to white light. We now report studies on (*E,E*)-dibenzylidenesuccinic thioanhydride, the first photochromic thioanhydride. This compound has been prepared by the reaction of (*E,E*)-dibenzylidenesuccinic acid dichloride with sodium sulfide nonahydrate in a solid-liquid system in dichloromethane in the presence of a phase transfer catalyst, and has been shown to be the (*E,E*)-isomer (**1b**) by X-ray diffraction analysis. On irradiation at 366 nm, the (*E,E*)-thiofulgide isomerize and cyclize in a similar fashion as **1a**. Cyclization to the red 1,8a DHN occurs instantaneously on exposure to UV light, and although no kinetic studies were done, the color change of the (*E,E*)-thiofulgide (**1b**) to the red form (1,8a DHN) was found to be more sensitive than for either the corresponding (*E,E*)-fulgide (**1a**) or (*E,E*)-fulgimide (**1c**) in solution as well as in crystals. The charge distribution in the 4n + 2 π-system (6π) that is involved in the electrocyclic ring closure reaction would be expected to have a marked influence on the sensitivity. Davies [5], as well as Fleischhauer

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[6], has shown that thioanhydride groups (as anhydride groups) are electron withdrawing when bonded to atoms in a π -electron system and cause a greater degree of charge deficiency in the π -system than their anhydride analogues.

This problem was investigated by NMR spectroscopy and semiempirical molecular orbital calculations using the AM1 method, which gives superior results [7] to MNDO or MINDO/3 in the study of crowded molecules. The electron densities calculated with AM1 were also correlated with the ^{13}C NMR chemical shifts of the three (*E,E*)-compounds, **1a**, **1b**, and **1c**. Substitution of the oxygen in **1a** with a larger atom (sulfur) causes a greater amount of twisting in the five-membered ring. This effect also seems to decrease the overlapping of the phenyl rings, and the subsequent mutual shielding of the phenyl protons is slightly reduced, as is evident from the ^1H NMR spectra. Comparison of the crystal structures of **1a** [8] and **1c** [9] with that of the title compound reported here shows only slight differences in bond lengths and bond angles of the 1,4-diphenyl-1,3-butadiene system, with more significant differences in the torsion angles. The observed increase in sensitivity and/or the reactivity of the (*E,E*)-thiofulgide therefore seems to be a combination of electronic and structural changes within the conjugated 1,4-diphenyl-1,3-butadiene system (Figure 1).

RESULTS AND DISCUSSION

The photochemical reactions of the fulgide (**1a**) [3] and the fulgimide (**1c**) [4] have been fruitfully studied before. The marked bathochromic shift in the thioanhydride (**1b**) compared to the anhydride (**1a**) and the imide (**1c**) (Figure 2a) could possibly be attributed to an increase in the conjugation in the chromophore due to the better resonance stabilization of the thioanhydride group. In the case of the thiofulgide (**1b**), irradiation at 366 nm in benzene, dichloromethane, or chloroform has been shown to cause isomerization and cyclization that is similar to its fulgide (**1a**) analogue. The red color change on cyclization has been attributed to the formation of the 1,8a DHN, as in the case of the fulgide (**1a**), and was also characterized by a bathochromic shift of 39.8 and 28 nm in comparison with the 1,8 DHNs of **1a** and **1c** respectively (Figure 2b).

On irradiation at 366 nm under a nitrogen atmosphere for 2 h, the 1,8a DHN is converted irreversibly to the colorless 1,4 DHN (**7b**). This is much faster than in both **1a** and **1c**, which require prolonged periods of irradiation for a quantitative conversion to the irreversible photoproducts. In the proton NMR the 1,4 DHN (**7b**) gives a doublet of doublets at 4.44 ppm for H-4 and a doublet of doublets at 4.45 ppm for H-4', due to the unequivalency of these two hydrogens. The geminal coupling for

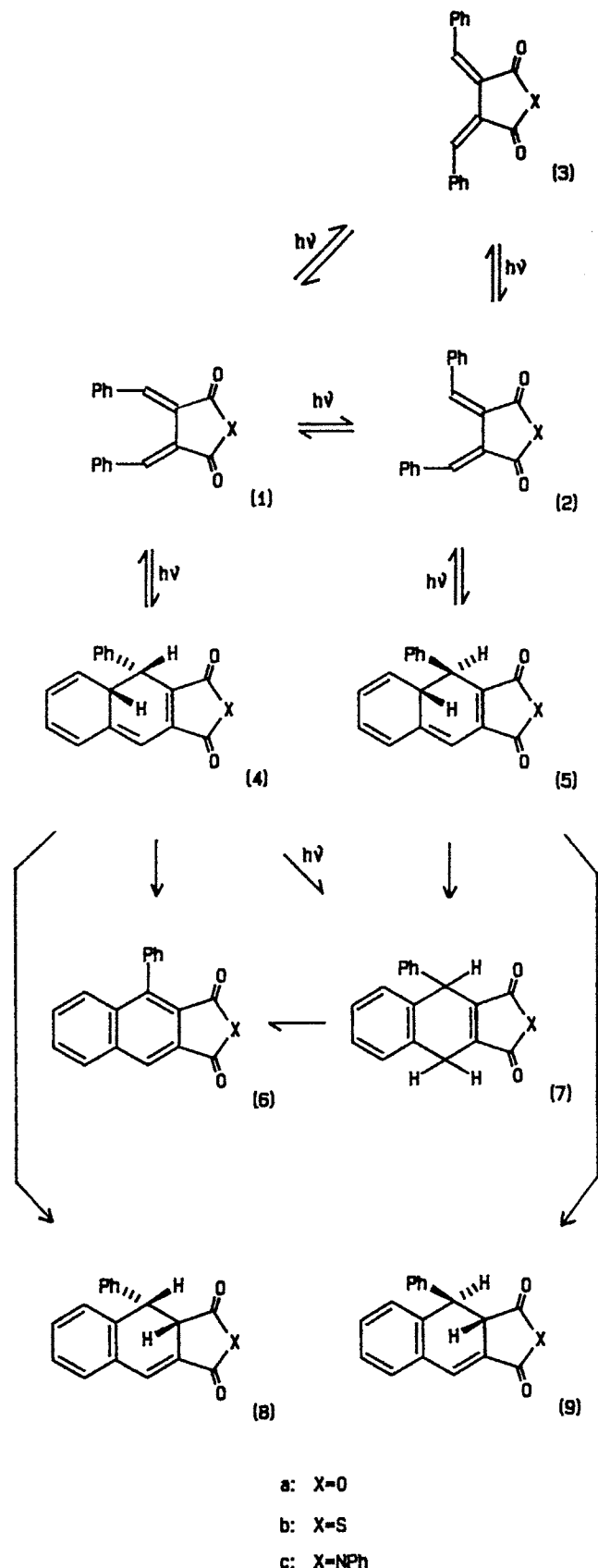
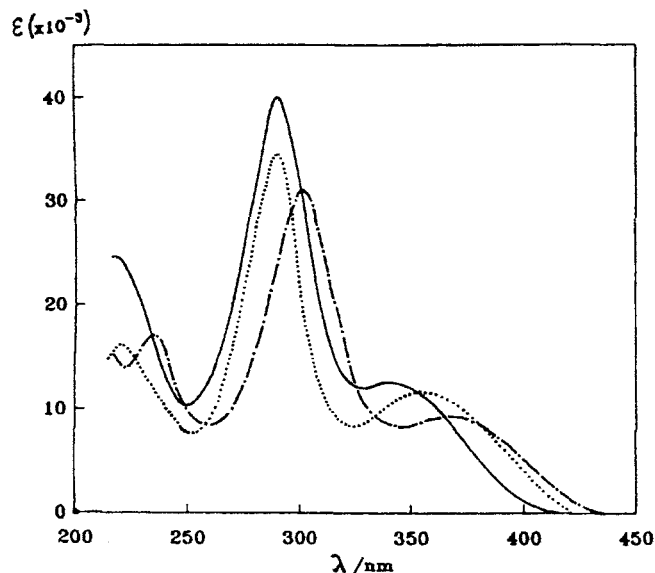
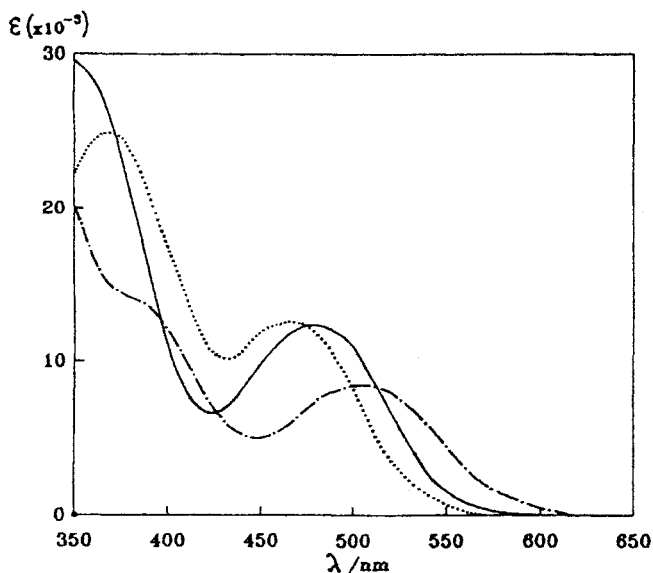


FIGURE 1 The reaction scheme of the photochemical rearrangement of **1a**, **1b** and **1c**.



A



B

FIGURE 2 The absorption spectra of **1a** (.....), **1b** (— · —), and **1c** (—) in dichloromethane before (A) and after (B) irradiation at 366 nm to give the photostationary state.

these two hydrogens is 14.4 Hz. The triplet at 5.25 ppm for H-1 is caused by the homoallylic coupling (3.6 Fz) between H-4, H-4', and H-1, as also seen from the 2-D COSY ^1H - ^1H spectrum. On prolonged irradiation (3 h) in the atmosphere the thiofulgide (**1b**) undergoes dehydrogenation, affording the fully aromatic, colorless 1-phenylnaphthalene-2,3-carboxylic thioanhydride, which is identical (mp, ^1H

NMR, ^{13}C NMR, and IR) to the independently synthesized compound.

The competing thermal 1,5H shift reaction leading to the *cis*- and *trans*-1,2-dihydronaphthalene derivatives such as (**8**) and (**9**) have not been investigated here, although some preliminary results indicate the formation of these compounds in a competing reaction. In benzene or ortho-dichlorobenzene the 1,5H shift reaction to the 1,2-DHN should be predominant.

Crystal Structure

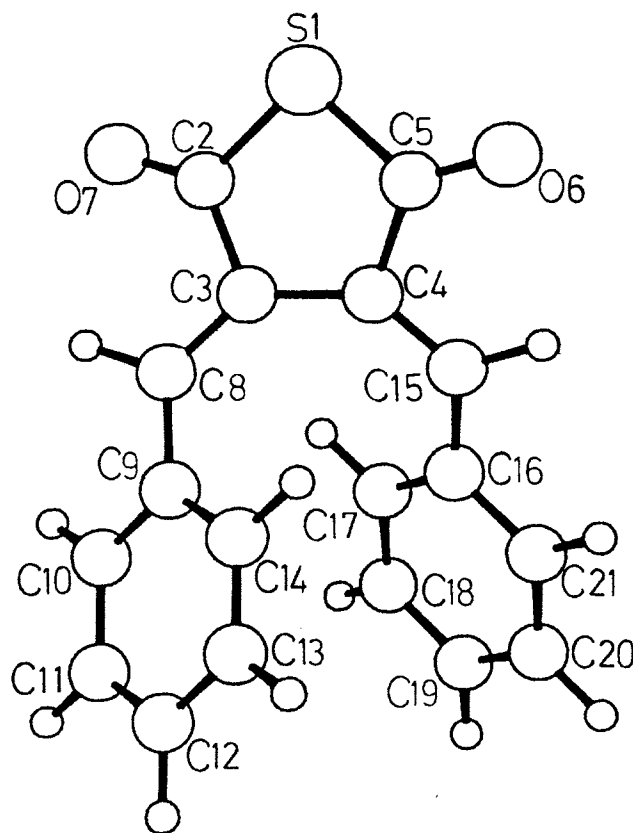
The structure of **1b** was determined by X-ray crystallography and compared to the known structures of **1a** and **1c** [8], [9]. Selected molecular parameters, relevant to the discussion of the structural relationship of compounds **1a**, **1b**, and **1c** are listed in Table 1. Figure 3 shows the atomic numbering and ORTEP drawing of **1b**.

The most significant differences in the structure of **1b** in comparison to the structures of **1a** and **1b** were found in the five-membered succinic ring. Because of the larger outer valence shell of the sulfur in **1b**, the bond lengths S(1)–C(2) and S(1)–C(5) are increased to 1.794(6) and 1.772(7) Å respectively, compared to the corresponding bond lengths for **1a** and **1c** (see Table 1). This is coupled with an increase in the endocyclic bond angles, S(1)–C(2)–C(3), S(1)–C(5)–C(4), C(2)–C(3)–C(4) and C(5)–C(4)–C(3) relative to the anhydride (**1a**) and the *N*-phenylimide (**1c**) (see Table 1), and a decrease in the C(2)–S(1)–C(5) bond angle, ($93.2(3)^\circ$ in **1b**, $110.3(2)^\circ$ in **1a**, $112.2(3)^\circ$ in **1c**). A comparison, in terms of endocyclic torsion angles (Table 1), clearly indicates a greater amount of twisting of the five-membered succinic ring in the thioanhydride (**1b**). In all three structures, the steric interactions experienced by the phenyl groups impose severe steric strain upon the molecules. Twisting of the C(3)–C(4) bond, aiming to maximize the mutual intramolecular distance of the interacting phenyl groups, is comparable for all three compounds (the torsion angle C(8)–C(3)–C(4)–C(15), being $32.5(5)^\circ$ in **1a**, $31.2(10)^\circ$ in **1b** and $37.9(3)^\circ$ in **1c**).

The relief brought about by the increase of the exocyclic bond angles, C(8)–C(3)–C(4) and C(15)–C(4)–C(3), is however, slightly reduced in **1b**, due to the increase in the C(2)–C(3)–C(4) and C(5)–C(4)–C(3) (see Table 1) endocyclic bond angles relative to **1a** and **1c**. The increase in the torsion angles C(4)–C(15)–C(16)–C(17), C(3)–C(8)–C(9)–C(14) and the decrease in the torsion angles C(3)–C(8)–C(9)–C(10), C(4)–C(15)–C(16)–C(21) (see Table 1) in **1b** relative to **1a** and **1c** are compensating somewhat for the "loss" in steric relief by bond angle enlargement. This change in torsion angles reduces the planarity of the [O(7)–C(2)–C(3)–C(8)–C(9) to C(14)] and [O(6)–C(5)–C(4)–C(15)–C(16) to C(21)] systems in **1b** even more. The carbonyl oxygens [O(6) and

TABLE 1 Selected Molecular Parameters of **1a**, **1b**, **1c** Determined by X-ray Diffraction; Standard Deviation in Parentheses. For Atom Numbering See Figure 3.

	Bond Distance (Å)		
	1a	1b	1c
X(1)–C(2)	1.391(3)	1.794(6)	1.392(2)
X(1)–C(5)	1.399(3)	1.772(7)	1.392(2)
C(2)–O(7)	1.185(3)	1.196(7)	1.203(2)
C(5)–O(6)	1.184(3)	1.202(7)	1.203(2)
C(2)–C(3)	1.490(3)	1.484(8)	1.496(2)
C(5)–C(4)	1.486(3)	1.499(8)	1.496(2)
C(3)–C(4)	1.452(3)	1.476(8)	1.452(2)
C(3)–C(8)	1.338(3)	1.345(7)	1.349(2)
C(4)–C(15)	1.339(3)	1.329(8)	1.349(2)
C(8)–C(9)	1.453(3)	1.464(8)	1.460(2)
C(15)–C(16)	1.456(3)	1.457(8)	1.460(2)
	Angle (°)		
	1a	1b	1c
X(1)–C(2)–C(3)	108.2(2)	110.4(5)	106.7(1)
X(1)–C(5)–C(4)	108.0(2)	111.0(5)	106.7(1)
C(2)–C(3)–C(4)	105.9(2)	111.4(5)	106.1(1)
C(5)–C(4)–C(3)	105.7(2)	110.6(5)	106.1(1)
C(3)–C(4)–C(15)	135.7(2)	133.9(6)	136.1(1)
C(4)–C(3)–C(8)	136.9(2)	133.4(6)	136.1(1)
C(3)–C(8)–C(9)	130.7(2)	130.8(6)	129.7(1)
C(4)–C(15)–C(16)	129.1(2)	130.6(6)	129.7(1)
C(2)–X(1)–C(5)	110.3(2)	93.2(3)	112.2(1)
X(1)–C(5)–C(6)	120.5(2)	121.9(5)	125.1(1)
X(1)–C(2)–O(7)	120.8(2)	120.7(5)	125.1(1)
C(3)–C(2)–O(7)	131.2(3)	128.7(6)	128.2(1)
C(4)–C(5)–O(6)	131.5(3)	126.9(6)	128.2(1)
C(2)–C(3)–C(8)	116.8(2)	114.9(6)	117.0(1)
C(5)–C(4)–C(15)	118.0(2)	115.4(6)	117.0(1)
	Torsion Angle (°)		
	1a	1b	1c
X(1)–C(2)–C(3)–C(8)	161.2(2)	158.0(5)	158.7(3)
O(7)–C(2)–C(3)–C(8)	–17.1(4)	–16.5(9)	–20.4(3)
X(1)–C(5)–C(4)–C(15)	160.1(2)	161.7(5)	158.7(3)
O(6)–C(5)–C(4)–C(15)	–17.7(4)	–13.1(10)	–20.4(3)
C(2)–C(3)–C(8)–C(9)	–167.2(2)	–168.0(6)	–166.8(3)
C(5)–C(4)–C(15)–C(16)	–164.4(2)	–169.6(6)	–166.8(3)
C(3)–C(8)–C(9)–C(10)	–159.2(3)	–149.2(6)	–159.4(3)
C(3)–C(8)–C(9)–C(14)	24.7(4)	32.7(10)	24.7(3)
C(4)–C(15)–C(16)–C(17)	28.3(4)	31.2(10)	24.7(3)
C(4)–C(15)–C(16)–C(21)	–154.6(3)	–153.6(7)	–159.4(3)
C(15)–C(4)–C(3)–C(8)	32.4(5)	31.3(11)	37.9(3)
C(15)–C(4)–C(3)–C(2)	–155.8(3)	–156.2(6)	–153.0(3)
C(8)–C(3)–C(4)–C(5)	–157.1(3)	–152.6(7)	–153.6(3)
C(3)–C(4)–C(15)–C(16)	5.2(5)	6.3(12)	0.0(3)
C(4)–C(3)–C(8)–C(9)	4.0(5)	4.4(11)	0.0(3)
O(6)–C(5)–X(1)–C(2)	177.2(3)	–179.7(5)	–176.2(3)
C(5)–X(1)–C(2)–C(3) ^a	4.4(3)	6.1(6)	4.5(3)
X(1)–C(2)–C(3)–C(4) ^a	–12.3(3)	–16.0(7)	–12.4(3)
C(2)–C(3)–C(4)–C(5) ^a	14.7(3)	19.9(8)	14.9(3)
C(3)–C(4)–C(5)–X(1) ^a	–12.4(3)	–15.2(7)	–12.4(3)
C(4)–C(5)–X(1)–C(2) ^a	–5.0(3)	5.2(6)	4.5(3)

^aFive-membered ring endocyclic torsion angles.**FIGURE 3** A prospective view of the molecule **1b** with atomic numbering.

O(7)] deviate by 0.4(2) Å and –0.3(2) Å respectively from these planes and both α -carbons [C(4) and C(3)] deviate by –0.4(2) Å and 0.5(2) Å respectively. In the phenyl rings, the meta carbons [C(18) and C(13)] show the most significant deviation [0.2(2) Å and 0.3(2) Å respectively]. This deviation is responsible for the lowering of conjugation (resonance effect) over the mentioned systems, as indicated in the ¹³C NMR spectra.

The somewhat larger C(3)–C(4) bond length [1.476(8) Å in **1b** and 1.452(3) Å in both **1a** and **1c**] in **1b** could be due to the increased puckering of the five-membered ring, which would tend to reduce the conjugation. This bond is shorter than the corresponding bond in succinic thioanhydride (1.514 Å) and longer than in maleic thioanhydride (1.342 Å), as calculated by the AM1 MO method (7). This partial double bond character of the C(3)–C(4) bond is expected, as in the case of **1a** and **1c**, due to the conjugation over the 1,4-diphenyl-1,3-butadiene system. Similarly to **1c**, the C(5)–O(6) and C(2)–O(7) bonds in **1b** [1.196(7) Å and 1.202(7) Å] are longer than the corresponding bonds in **1a** (see Table 1).

The aryl rings [C(9) to C(14)] and [C(16) to C(21)] in **1b**, having their plane normals inclined at a 30.4° angle, show little deviation from the anhydride (**1a**) [8] and *N*-phenylimide (**1c**) [9] structures, in which

the plane normals are inclined at an angle of 35° and 34° respectively.

¹H NMR Spectra

The chemical shift values for all hydrogen atoms in compounds **1a**, **1b**, and **1c** are given in Table 2.

Unambiguous assignments were made with the help of the 2-D COSY technique. The mutual shielding of the aromatic hydrogens by the benzene rings in the *E,E*-configuration of compound **1a** have been previously discussed [3] in detail. The shielding effect, compared to the strain-free *E*-cinnamic anhydride, was shown to increase in the order ortho > meta > para, as the distances between the corresponding positions in the ring increase. The aromatic protons in the 1,4-diphenyl-1,3-butadiene system in compounds **1b** and **1c** follow the same trend as in **1a**. The shielding of the ortho protons in **1b** is slightly decreased, as indicated by a down-

field shift of 0.24 ppm compared to **1a**. This is due to the change in the torsion angles around the C(8)–C(9) and C(15)–C(16) bonds (as discussed earlier), which decrease the distance between the ortho protons and effectively move these hydrogens slightly out of the shielding section of the magnetic field induced by the opposite ring. The *N*-phenyl protons in **1c** are moved significantly downfield from the aromatic protons in the *E,E*-configuration (see Table 2). This also illustrates the shielding effect the two aromatic rings have on each other, as opposed to the strain-free *N*-phenyl ring. The upfield shift of the β -hydrogen in **1b** relative to **1a** and **1c** could be attributed to the higher electron density at the β -carbon, as determined by the ¹³C chemical shifts. Steric interactions, however, would be expected to have a greater influence on the shifts, and it is possible that the β -hydrogen is lying in a different part of the shielding anisotropy of the adjacent oxygen.

¹³C NMR Spectra

Chemical shift data, together with the net atomic charges as calculated by AM1 method for individual carbon atoms in compounds **1a–1c**, are given in Table 3. Unambiguous assignment of ¹³C resonances was based on 2-D techniques (HETCOR) for protonated carbons and the SPT technique [10] for the quaternary carbons. Semiempirical correlations have assumed an important and valid role in ¹³C NMR. The quantitative relationship between chemical shift and electron density in a carbon atom has attracted particular interest [11]. Various classes of compounds have been investigated for which a linear dependence was assumed [12]. This assump-

TABLE 2 The Chemical Shifts (δ) of Olefinic and Aromatic Hydrogen Atoms in Substrates **1a–1c** (CDCl₃; 18°C)

Compound	1a	1b	1c
H $_{\beta}$	7.89	7.64	7.88
H $_{ortho}$	6.78	7.02	6.92
H $_{meta}$	6.83	6.88	6.83
H $_{para}$	7.12	7.06	7.07
<i>N</i> -phenyl			
H $_{ortho}$			7.50
H $_{meta}$			7.51
H $_{para}$			7.41

TABLE 3 ¹³C NMR Chemical Shifts^a and (in Parentheses) Net Atomic Charges^b for Carbon Atoms of Substrates **1a**, **1b** and **1c**. The Shielding Effects ($\Delta\delta$) of Selected Carbon Atoms Are Also Given.

Compound	1a	1b	1c
C $_{carbonyl}$	165.99 (0.331)	191.52 (0.137)	169.31 (0.349)
C $_{\alpha}$	119.29 (−0.146)	129.00 (−0.171)	122.43 (−0.133)
C $_{\beta}$	139.57 (0.000)	135.35 (0.002)	135.61 (−0.016)
C $_{ipso}$	133.78 (−0.080)	133.94 (−0.077)	134.67 (−0.073)
C $_{ortho}$	129.96 (−0.096)	130.30 (−0.097)	129.79 (−0.101)
C $_{meta}$	127.10 (−0.134)	127.56 (−0.135)	127.06 (−0.134)
C $_{para}$	130.75 (−0.107)	130.41 (−0.108)	129.46 (−0.110)
<i>N</i> -phenyl			
C $_{ipso}$			132.13 (0.059)
C $_{ortho}$			126.47 (−0.136)
C $_{meta}$			128.99 (−0.119)
C $_{para}$			128.29 (−0.139)
	1b–1a	1c–1a	
C $_{carbonyl}$	25.53	3.32	
C $_{\alpha}$	9.71	3.14	
C $_{\beta}$	−4.22	−3.96	

^a Shifts in ppm

^b Calculated by AM1 method

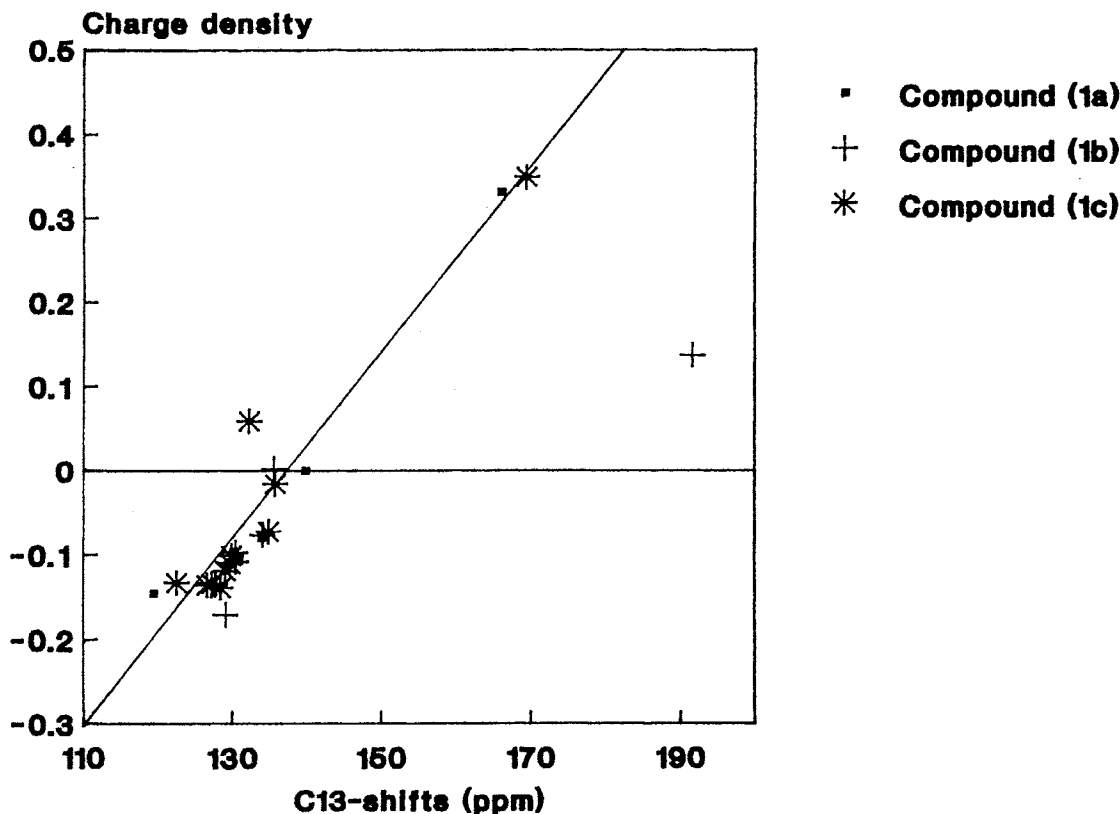
tion was tested for the three compounds **1a**, **1b**, and **1c**, whose net atomic charges were calculated by the AM1 method; compounds **1a** and **1c** show a reasonable linearity (Figure 4). Because this correlation is, in part, theoretically based, the extent to which the data fit the linear correlation depends on the method of calculation. The deviation from linearity for compound **1b** may therefore occur because AM1 is a fairly new method [7], and parametrization is not fully refined and tested, especially for sulfur, which has little experimental data available. The reported structure is indeed the first X-ray structure of a thioanhydride system.

In the following discussion it is assumed that the linear relationship between the chemical shift and electron density in **1a** and **1c** may be extended to the thiofulgide (**1b**). The most significant changes in chemical shifts for the series **1b**, **1c**, and **1a** are observed for C(carbonyl), C(α) and C(β) atoms. The chemical shift for the C(carbonyl) atoms increases in the order **1b** > **1c** > **1a** with the C(carbonyl) atoms of **1b** and **1c** being shifted downfield relative to **1a** by 25.53 ppm and 3.32 ppm respectively. The chemical shifts of carbonyl carbons and their heteroatom analogues (C=S, C=Se, C=N) increase with decreasing electronegativity [12]. This trend is attributed to the paramagnetic shielding term [13], in which the average excitation energy ΔE

decreases in the order O > N > S > Se, resulting in an increase in σ^{para} and a downfield shift. The chemical shift of the C(carbonyl) atoms in the anhydride (**1a**), *N*-phenylimide (**1c**) and thioanhydride (**1b**) follow the same trend and can be explained by a relative greater contribution from the mesomeric form III (see Figure 5), compared to form II.

The upfield shift of the C(carbonyl) atoms in these compounds compared with a ketone can also be explained by the greater contribution of the mesomeric form (III) relative to form (II). Owing to the contribution of the form (IV), the signals of the C(carbonyl) atoms are shifted even more to a high field relative to those in the corresponding saturated compounds [14]. The shifts for the C(α) atoms show a dependence similar to that of the C(carbonyl) chemical shift, **1b** > **1c** > **1a**, with the C(α) atoms of **1b** and **1c** being shifted downfield from **1a** by 9.71 ppm and 3.14 ppm respectively. This trend is inverted for the C(β) atoms, which show a decrease in chemical shift in the order **1a** > **1c** > **1b**, with the C(β) atoms of **1b** and **1c** being shifted upfield compared to **1a** by 4.22 ppm and 3.96 ppm respectively. The difference in the shielding of the C(α) atoms relative to the C(β) atoms (C(α) being most shielded) due to the polarization of the olefinic bond, which transmits the conjugation between the (donor) phenyl and (acceptor) carboxylic group, de-

FIGURE 4 The correlation between observed ^{13}C shifts and calculated electron densities. The points marked are the values for **1a**, **1b** and **1c**.



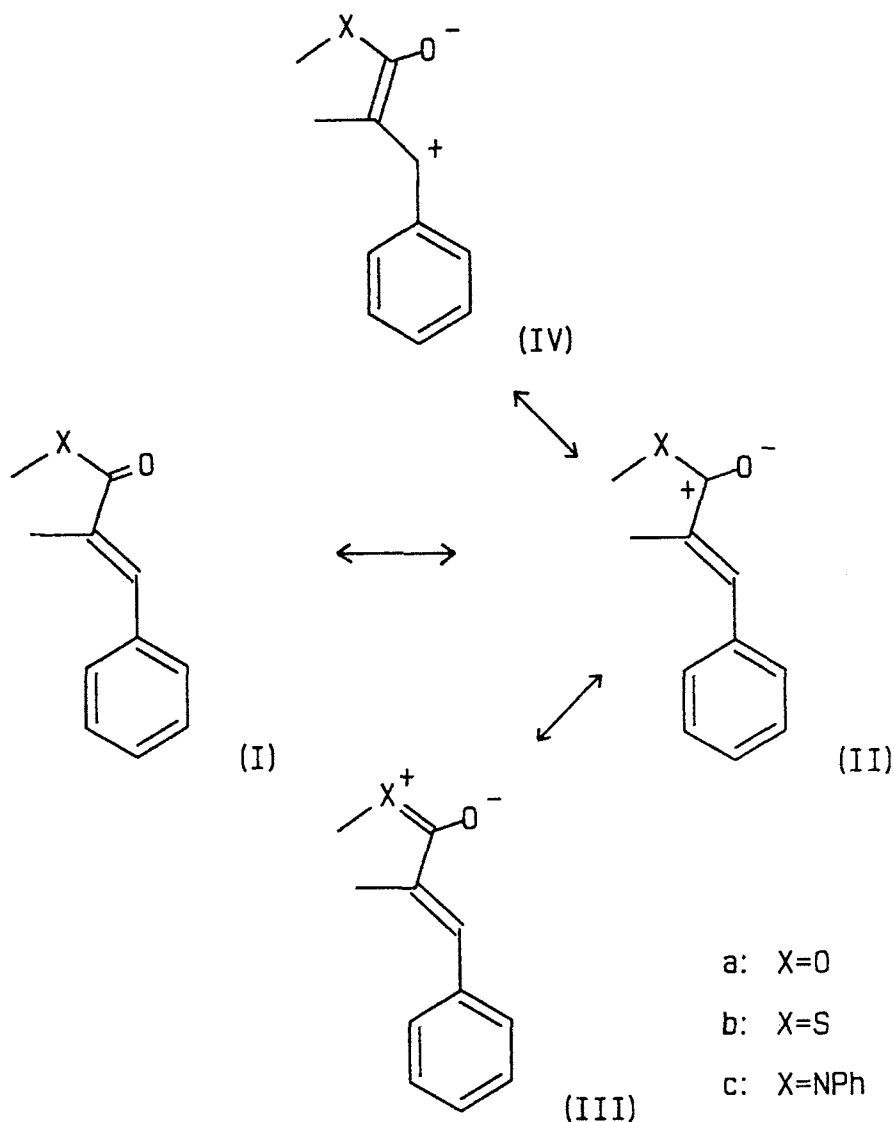


FIGURE 5 Resonance structures contributing to the ^{13}C shielding.

creases for the substituents in the order $\text{O} > \text{N} > \text{S}$, the $\Delta\delta$ values being 20.28 ppm, 13.18 ppm, and 6.35 ppm for **1a**, **1c**, and **1b** respectively. The electronic effects of substituents may be regarded as the sum of inductive and resonance effects, and in this case inductive effect is rationalized by the electronegativity of the substituent. As the electronegativity decreases in the order $\text{O} > \text{N} > \text{S}$, the thioanhydride group should have a weaker electron withdrawing effect by induction than either the *N*-phenylimide- (**1c**) or the anhydride (**1a**) groups and a stronger electron withdrawing effect by resonance due to the larger outer valence shell of sulfur. Due to the deviation from planarity of the $\text{O}(7)\text{--C}(2)\text{--C}(3)\text{--C}(8)$ and $\text{O}(6)\text{--C}(5)\text{--C}(4)\text{--C}(15)$ bond systems, the importance of the resonance effect over the olefinic bond seems to be reduced and the inductive or π -polarization mechanism may be the dominant substituent effect, thus accounting for the

observed decrease in polarization of the olefinic bond in **1b**.

The aromatic phenyl carbons do not exhibit any significant changes in their ^{13}C chemical shifts. The significantly higher and lower electron densities at $\text{C}(\beta)$ and $\text{C}(\alpha)$ respectively in the 1,4-phenyl-1,3-butadiene system of the thiofulgide (**1b**) and the greater "aromaticity" seem to be responsible for the apparent change in sensitivity. The electronic substituent effects of sulfur in **1b** therefore seem to be a more important factor in the cyclization reaction than the structural changes in the **1a**, **1b**, and **1c** series.

EXPERIMENTAL

Melting points are uncorrected. Measurements involved Gallenkamp melting point apparatus (mp), Bruker IFS 113v FT-IR (IR for dispersion in KBr),

Varian-CARY 2390 (UV-vis. in dichloro-methane solutions), Varian-MAT-212 double focusing direct inlet spectrometer (MS), FT Bruker AC 300 spectrometer (NMR in deuteriochloroform solutions). TLC was carried out on precoated silica gel plates (Merck F254). The solutions were irradiated at 366 nm, using a high pressure mercury lamp (OSRAM 400 Watt, without luminescent phosphorus coating), with a filter (type OX1, Chance Pilkington). Photoreactions were carried out in deuteriochloroform in appropriate atmosphere in sealed NMR tubes. Light petroleum refers to the fraction boiling in the range 80–100°C.

(*E,E*)-Dibenzylidenesuccinic Anhydride (**1a**)

The (*E,E*)-anhydride (**1a**) was prepared directly from crude acid, which was synthesized following the procedure given in the literature [14]. Yield 22%; yellow bipyrimal crystals; mp 206.1–207.1°C (from benzene; lit [3] mp 203°C); λ_{\max} (CH₂Cl₂): 357.8 ($\epsilon = 4101$), 290.4 ($\epsilon = 34420$); ν_{\max} : 1819.5 and 1766.1 (C=O), 1617.0, 1591.0, and 1573.2 (C=C—C=C). Detailed ¹H and ¹³C NMR assignments are given in Tables 2 and 3.

(*E,E*)-Dibenzylidenesuccinic Thioanhydride (**1b**)

The (*E,E*)-dibenzylidenesuccinic anhydride was converted to the (*E,E*)-2,2'-dibenzylidenesuccinic acid dichloride with PCl₅ as described in [15]. A solution of the (*E,E*)-acid dichloride (1.7 g; 5.13 mmol) and tetrabutylammonium bromide (0.07 g; 0.217 mmol) in dichloromethane (20 ml) was cooled to 0°C. Powdered sodium sulfide nonahydrate (1.3 g; 5.01 mmol) was added in portions during 30 min at 0°C with vigorous stirring. The reaction proceeded exothermically, and the mixture was allowed to heat by itself. After 4 h the stirring was stopped and the mixture filtered through "celite" 545. The mixture was then immediately passed through a short column of silica gel with dichloromethane as eluent to remove the catalyst. TLC showed that only two components were present in the product (yield 1.02 g). The required product was separated by chromatography of the crude products through a column of silica gel eluting with benzene-light petroleum (1:1 v/v). The (*E,E*)-thioanhydride (**1b**) was collected as the first yellow fraction and crystallized from chloroform to afford the pure (*E,E*)-dibenzylidenesuccinic thioanhydride (0.483 g; 32%) as intense yellow, light-sensitive crystals, mp 160.7–163.1°C, suitable for X-ray diffraction studies; m/z 293 (M⁺, 100%); λ_{\max} (CH₂Cl₂): 365 ($\epsilon = 9271$), 302.2 ($\epsilon = 31360$), 236.2 ($\epsilon = 17080$); ν_{\max} : 1721.2 and 1688.9 (C=O), 1600.7, 1592.5, and 1571.7 (C=C—C=C); detailed ¹H and ¹³C NMR assignments are given in Tables 2 and 3.

(*E,E*)-Dibenzylidene-*N*-phenylsuccinimide (**1c**)

The (*E,E*)-*N*-phenylimide [4] was obtained by boiling (4 h) a solution of the (*E,E*)-anhydride (**1a**) (5 g; 18.1 mmol) and aniline (1.69 g; 18.1 mmol) in benzene (50 ml) and refluxing the formed (*E,E*)-*N*-phenylsuccinamic acid (6.5 g) in acetyl chloride (50 ml). Removal of the acetyl chloride and crystallization from benzene gave the pure *N*-phenylimide (**1c**) (5.7 g; 90%) as pale yellow crystals, mp 201.7–202.4°C (lit. [4] 200–201°C); λ_{\max} (CH₂Cl₂): 337.2 ($\epsilon = 12700$), 290.6 ($\epsilon = 39980$), 219.8 ($\epsilon = 24800$); ν_{\max} : 1764.6 and 1704.3 (C=O), 1625.2, 1597.7, and 1576.0 (C=C—C=C); detailed ¹H and ¹³C NMR assignments are given in Tables 2 and 3.

1-Phenylnaphthalene-2,3-dicarboxylic Thioanhydride (**6b**)

The 1-phenylnaphthalene-2,3-dicarboxylic acid dichloride (1.6 g; 5.52 mmol), obtained from the reaction of the corresponding anhydride with phosphorus pentachloride (1.2 g; 5.76 mmol) [15] and tetrabutylammonium bromide (0.04 g; 0.14 mmol) in dichloromethane (20 ml), was treated with powdered sodium sulfide nonahydrate (1.33 g; 5.54 mmol) at 0°C. The product was separated as described for **1b**, and the thioanhydride (**4**) (0.62 g; 44%) was obtained from benzene-chloroform (1:1 v/v) as colorless needles, mp 227.4–228.2°C; λ_{\max} (CH₂Cl₂): 273.4 ($\epsilon = 57580$), 375.2 ($\epsilon = 4783$), 360.4 ($\epsilon = 3867$), 310.6 ($\epsilon = 7022$), 226.0 ($\epsilon = 24520$); ν_{\max} : 1726.5 and 1692.3 (C=O) 1611.7 and 1596.3 (C=C—C=C). ¹H NMR 8.51 (1H, s, H-4), 8.11 (1H, d, ³J 8.2 Hz, H-5), 7.72 (1H, ddd, ³J 8.1 Hz, ³J 6.6 Hz, ⁴J 1.5 Hz, H-6) 7.61 (1H, ddd, ³J 8.4 Hz, ³J 6.8 Hz, ⁴J 1.4 Hz, H-7), 7.68 (1H, dd, ³J 7.6 Hz, ⁴J 0.7 Hz, H-8), 7.29 (2H, m, H-2"), 7.53 (2H, m, H-3"), 7.53 (1H, m, H-4").

Rearrangement Reaction of the (*E,E*)-Thiofulgide (**1b**)

The (*E,E*)-thiofulgide (**1b**) (50 mg) in deuteriochloroform at 25°C under a nitrogen atmosphere, on irradiation, gave the 1,4-DHN as the major product that was not isolated. The 1,4-DHN showed the characteristic NMR signals at 4.44 (1H, dd, ⁵J 3.6 Hz, H-4), 4.45 (1H, dd, ⁵J 3.6 Hz, H-4') and 5.25 (1H, t, ⁵J 3.6 Hz, H-1) similar to the 1,4-DHN obtained by irradiation of the (*E,E*)-fulgide (**1a**).

The (*E,E*)-thiofulgide (**1b**) (500 mg) was irradiated (2 h) in chloroform (75 ml) in atmosphere. The solvent was removed and the residue was chromatographed on silica gel eluting with benzene-light petroleum (2:1 v/v). The front-running fractions yielded the 1-phenylnaphthalene-2,3-dicarboxylic thioanhydride (**6a**) (364 mg; 72%), which was crystallized from benzene-chloroform (1:1 v/v) to afford colorless needles, identical (mp, UV, IR,

¹H NMR) to the independently synthesized thioanhydride (**6b**).

CRYSTALLOGRAPHIC ANALYSIS

The data were collected at room temperature with a CAD4-diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The dimensions of the crystal used were $0.46 \times 0.50 \times 0.22 \text{ mm}$. An $\omega:2\theta$ -scan was employed. The ω -scan angle changed as $(0.85 + 0.35 \tan \theta)$ degrees, the horizontal aperture as $(1.12 + 1.05 \tan \theta) \text{ mm}$, limited to 1.3–5.0 mm. The vertical slit was fixed to 4 mm. Data were collected in the region $3 \leq \theta \leq 25^\circ$, corresponding to $0 \leq h \leq 15$, $0 \leq k \leq 17$ and $-8 \leq l \leq 8$. A variable scan speed was used with a maximum of $8.3^\circ/\text{min}$ and a minimum corresponding to 50 sec measuring time per reflection. Of the 2733 reflections measured, 1859 were observed ($I > 2\sigma(I)$). The data were checked every hour for crystal decomposition, and every 200 reflections for changes in orientation. Reflections were corrected for Lorentz and polarization effects, and for absorption using an empirical method involving ψ -scans (average transmission 96.8%). The structure was solved with direct methods [16] and refined anisotropically [17] using a full matrix method and $1/\sigma^2$ (F)-weights. All hydrogen atoms were placed on calculated positions ($r_{\text{CH}} = 108 \text{ \AA}$, $\theta_{\text{HCH}} = 109.5^\circ$), and refined with a common isotropic temperature factor $U = 0.080(6) \text{ \AA}^2$. The maximum electron density in a final Fourier map was 0.38 e/\AA^3 . The structure converged to $R = 0.089$ and $wR = 0.085$ for 1859 reflections and 191 variables.

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