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CYCLOADDITION REACTIONS OF THE ANHYDRO-4-HYDROXYTHIAZOLIUM HYDROXIDE SYSTEM WITH DIMETHYL MALEATE AND DIMETHYL FUMARATE

X-RAY DETERMINATION OF THE EXO STRUCTURE OF THE CYCLOADDUCTS

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Abstract—The relative configuration of the carbons bearing the ester groups in the cycloadducts of anhydro - 4 - hydroxythiazolium hydroxides with dimethyl maleate and dimethylfumarate is revised in the light of an X-ray crystallographic analysis. Steric effects are considered to account for the preferred exo approach of the dipole and the dipolarophile.

4-Hydroxy thiazoles **1a** have been shown to undergo ready cycloadditions with dimethylmaleate and dimethylfumarate via the mesoionic tautomeric forms **1b**, to give the *cis* cycloadducts **2a**, **2b** and **2c**, **2d**[1,2]. Anhydro - 4 - hydroxythiazolium hydroxide system **3** reacts with these same dipolarophiles but generally gives rise to but one cycloadduct in each case, **4** or **5**[3,4] (Table 1). The coupling constant $J_{H_4H_5}$ shows unambiguously that the compounds **4** and **5** are *cis* cycloadducts. However, it is more difficult to know the relative configuration of the carbons 4 and 5. It has been postulated that the difference in chemical shift between the protons from *exo* to *endo* was due to the deshielding effect of the sulfide bridge. As a consequence, the chemical shifts observed for the H_4 and H_5 protons have been rationalized with protons in *exo* configuration in the cycloadduct of dimethylmaleate with the mesoionic thiazole **3**, (X = H, R = Ph) while a structure **5b** was assigned to the cycloadduct of dimethylfumarate with **3** (X = H, R = Ph).[3] However, we have noticed that the difference in chemical shift between *endo* and *exo* protons may be very small or even nill: for instance the same chemical shift has been observed for the proton H_4 *exo* in **2a** and H_4 *endo* in **2b**.[2]

In order to ascertain the relative configurations at carbons 4 and 5 of the cycloadducts, we have undertaken an X-ray diffraction study of compound **4** (X = Cl, R = Ph).

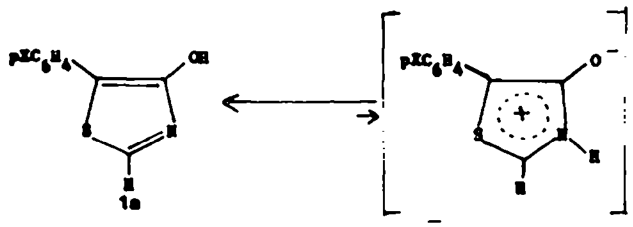
The S–C(3) and S–C(6) bond lengths of 1.833 and 1.835 Å are equal and correspond to a S–C(sp^3) bond.[5] The C(3)–S–C(6) bond angle (80.8°) is considerably smaller than the mean value of 90 ± 2° for various 5-membered heterocycles like thiazole systems. This is almost certainly due to the strain in the bridged-ring conformation. The same factor may lengthen the C(4)–C(5) bond whose distance is 1.581 Å and the C(6)–N bond (1.489 Å) which is significantly longer than the mean value of 1.411 Å.[6] However, the C(4)–C(5) bond may also be stretched by the ester–ester repulsion as both ester groups are oriented in the same direction. The non-bonded intramolecular distances 0(41) . . 0(51) and 0(42) . . 0(52), which are 3.301 and 3.253 Å respectively, indicate that these pairs of atoms are in close contact.

X-Ray discussion

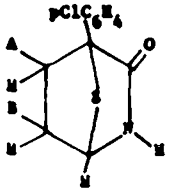
The molecular structure and atom labeling scheme are presented as a stereoscopic view in Fig. 1. The unit-cell packing is given in Fig. 2. A survey of the bond lengths

Table 1. Cycloadducts from 3 and dimethyl maleate or dimethyl fumarate

Dipolarophile	Dipôle	No. of isomers	Structure
	1b, X = Cl	2	**2a** 60%; **2b** 40%
Dimethyl maleate	**3**, X = H; R = Ph	1	**4** (CO_2CH_3 *exo*)
	3, X = Cl; R = Ph	1	**4** (CO_2CH_3 *exo*)
	3, X = Cl; R = CH_2Ph	1	**4** (CO_2CH_3 *exo*)
	1b, X = Cl	2	**2c** 60%; **2d** 40%
Dimethyl fumarate	**3**, X = H; R = Ph	1	**5a**
	3, X = Cl; R = Ph	1	**5a**
	3, X = Cl; R = CH_2Ph	2	**5a** (70%); **5b** (30%)

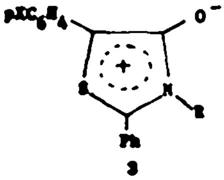


1a 1b

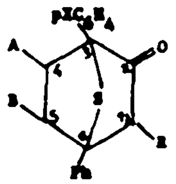


2

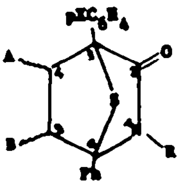
A = B = CO_2CH_3
2a: A,B *endo*
2b: A,B *exo*
2c: A *exo*, B *endo*
2d: A *endo*, B *exo*



3

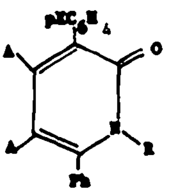


4(A,B *exo*)
(The numbering of Fig. 1 is used)



5

5a A *endo* B *exo*
5b A *exo* B *endo*



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and angles shown in Table 5 confirms the molecular structure. The crystal structure consists of discrete molecular units with no significantly short intermolecular distances. Although it is the first structure of this type of compound (so far as we know), the pattern of distances and angles does not show unusual features.

The plane through the atoms S, C(3) and C(6) makes an angle of 124.7° with the best plane through the atoms N, C(2), C(3) and C(6) and an angle of 122.5° with the best plane through the atoms C(3), C(4), C(5) and C(6). Phenyl rings C(11) . . . C(16) and C(61) . . . C(66) are perfectly planar with deviations from the plane of less than 0.008 Å and 0.010 Å respectively. The mean C–C bond distances are 1.382 (10) Å and 1.383 (10) Å, and the mean C–C–C angles are 120.0(7)° and 120.0(4)°. The deviations from the best plane in the C(31) . . . C(36) phenyl ring are −0.020, 0.007, 0.012, −0.019, 0.006 and 0.013 Å respectively, mean bond distance and angle is 1.380(10) Å and 120.0(16)°. A summary of best planes and dihedral angles is given in Table 6 to describe the complete conformation of the molecule.

Structure of the other cycloadducts 4 and 5

δ_{OCH_3} observed for the compound 4 (X = Cl, R = Ph) are very similar to those observed for the other compounds 4 listed in Table 7. As the X-ray study has established the *exo* position of the two ester groups in the compound 4 (X = Cl, R = Ph) it seems reasonable to

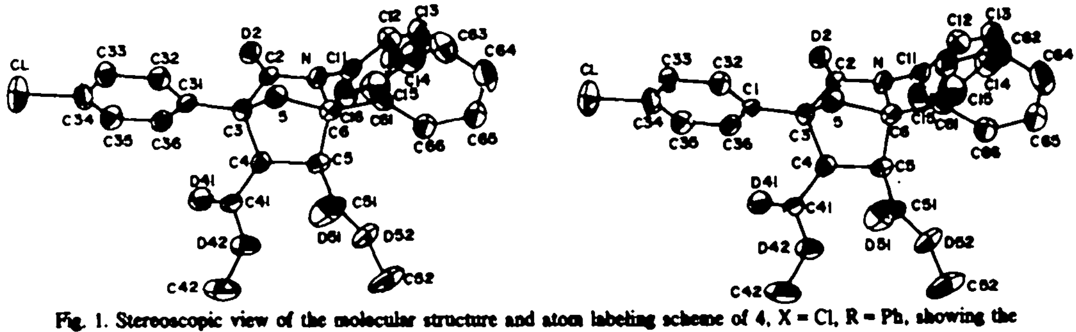

Fig. 1. Stereoscopic view of the molecular structure and atom labeling scheme of 4, X = Cl, R = Ph, showing the thermal ellipsoids at 50% probability.

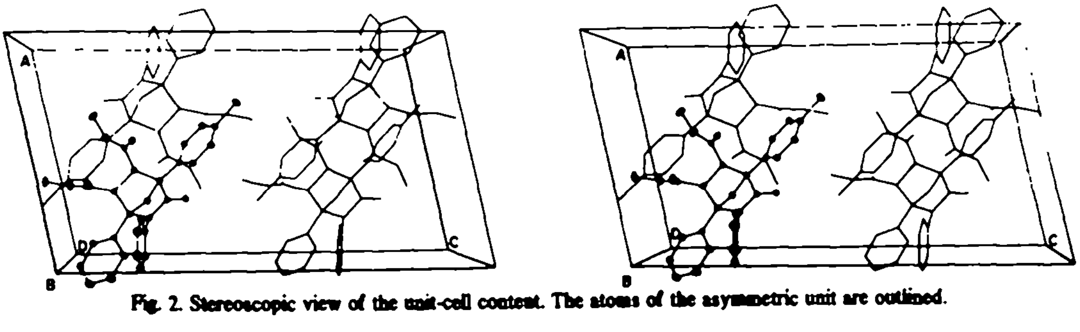

Fig. 2. Stereoscopic view of the unit-cell content. The atoms of the asymmetric unit are outlined.

Table 2. Crystal data

$C_{27}H_{22}ClNO_5S$	F.W. 507.997
Monoclinic	Space group $P2_1/c$
$a = 11.826(2)$ Å	$Z = 4$
$b = 10.128(2)$ Å	$D_c = 1.39\ \mathrm{g\,cm^{-3}}$
$c = 20.701(3)$ Å	$\lambda(\mathrm{Cu}K_\alpha) = 1.5418$ Å
$\beta = 101.6(1)°$	$\mu = 25.15\ \mathrm{cm^{-1}}$
$V_c = 2429$ Å^3	$\mu R \sim 0.25$

Table 3. Final fractional coordinates (× 10^4) of nonhydrogen atoms

Atom	x	y	z
Cl	7263(2)	4236(2)	5046(1)
S	2729(1)	4417(2)	2265(1)
O(2)	2723(4)	1358(5)	3222(2)
O(41)	5519(4)	4315(5)	2224(2)
O(42)	5675(4)	2882(5)	1516(2)
O(51)	3523(5)	4508(5)	860(2)
O(52)	3384(4)	2565(5)	347(2)
N	1844(4)	2065(5)	2189(2)
C(11)	1138(6)	919(7)	1980(3)
C(12)	−65(7)	1025(9)	1827(4)
C(13)	−719(8)	−84(13)	1614(4)
C(14)	−193(11)	−1275(13)	1559(5)
C(15)	993(9)	1388(10)	1718(5)
C(16)	1653(7)	−277(8)	1921(4)
C(2)	2699(5)	2041(7)	2742(3)
C(3)	3638(5)	3048(6)	2647(3)
C(31)	4498(5)	3336(6)	3265(3)
C(32)	4473(6)	4485(7)	3608(3)
C(33)	5308(6)	4772(6)	4164(3)
C(34)	6178(6)	3865(8)	4363(3)
C(35)	6203(6)	2679(7)	4046(3)
C(36)	5358(6)	2413(7)	3499(3)
C(4)	4143(5)	2496(6)	2057(3)
C(41)	5186(6)	3301(7)	1956(3)
C(42)	6663(8)	3346(9)	1345(5)
C(5)	3122(5)	2530(7)	1433(3)
C(51)	3388(6)	3338(8)	866(3)
C(52)	3627(9)	3202(10)	−241(4)
C(6)	2094(6)	3076(7)	1714(3)
C(61)	1013(5)	3481(7)	1224(3)
C(62)	273(6)	4412(8)	1400(3)
C(63)	−752(7)	4708(8)	969(4)
C(64)	−1046(6)	4072(9)	370(4)
C(65)	−326(7)	3138(8)	197(3)
C(66)	703(6)	2820(8)	625(3)

assign the structure 4 (CO_2CH_3 *exo*) to all these compounds which differ by the substituants X and (or) R only.

The cycloadduct of dimethylmaleate and anhydro - 4 - hydroxythiazolium hydroxide 3 (X = H, R = Ph) has been epimerized with sodium methoxide into a *trans* diester 5 (during this isomerization some pyridone 6, X = H, R = Ph was also obtained).[3] The epimerization was thought to occur at carbon 4 due to the expected acidity of the 4 proton. The ester groups were assumed to be *endo* in the starting cycloadduct, so the structure 5b was attributed to this *trans* diester.[3] As the X-ray study demonstrates the *exo* position of the ester groups in 4 (X = H, R = Ph) the *trans* diester 5 (X = H, R = Ph) obtained via sodium methoxide epimerization of 4 (X = H, R = Ph) must be 5a and not 5b. The same reactions (epimerization and pyridones 6 formation) occur with all the *cis* diesters 4 listed in Table 7 and we assign the structure 5a to the *trans* diesters obtained in this way.

Table 4. Calculated fractional coordinates (× 10^4) for hydrogen atoms

Atom	x	y	z
H(C12)	−472	1943	1873
H(C13)	−1632	−13	1493
H(C14)	−703	−2116	1394
H(C15)	1394	−2315	1685
H(C16)	2566	−351	2031
H(C32)	3801	5173	3446
H(C33)	5277	5664	4428
H(C35)	6861	1979	4218
H(C36)	5362	1496	3252
H(C4)	4398	1502	2157
H(C42)	6388	4288	1152
H′(C42)	7296	3463	1783
H″(C42)	7053	2853	994
H(C5)	2926	1554	1262
H(C52)	2997	3947	−385
H′(C52)	4455	3643	−113
H″(C52)	3625	2586	−655
H(C62)	489	4897	1862
H(C63)	−1315	5429	1101
H(C64)	−1830	4307	43
H(C65)	−554	2653	−265
H(C66)	1249	2078	495

Discussion of the endo-exo *orientation of the cycloaddition*

Compounds 2, 4 and 5 are not isomerized under the cycloaddition conditions. So they are the kinetic products of the reaction. 1,3-Dipolar cycloadditions are known to give rise preferentially to the *endo* cycloadducts. This kind of approach of the dipole and the dipolarophile is still observed with the labile monosubstituted mesoionic thiazoles 1b, but the trisubstituted mesoionic thiazoles 3 yield the cycloadducts with the least steric interactions. In one case, 3 (X = Cl, R = CH_2Ph) gives two isomers 5a and 5b. In agreement with the preponderant effect of the steric interactions, 5a is the major isomer (Table 1). The formation of two isomers in this case may reflect similar steric interactions in either *endo* or *exo* approaches of the dipole and dipolarophile.

In conclusion, it appears that the *endo-exo* orientation of the cycloaddition of dimethylmaleate or dimethylfumarate with anhydro - 4 - hydroxythiazolium hydroxide 3 is closely related to steric factors. The unique *cis* cycloadduct generally obtained is the one with the least steric interactions.

EXPERIMENTAL

IR spectra were measured in CCl_4 on a Perkin Elmer 225 spectrophotometer. ^1H NMR spectra were recorded on a Jeolco JNM MH 100 Spectrometer using a chloroform-d solvent and TMS as internal standard; chemical shifts are reported in δ (ppm) units. Mass spectral data were obtained on Varian Mat 311 spectrometer.

Preparation of the cycloadducts 4, 5a and 5b. Compound 3 (5 mmoles) and dimethylmaleate or dimethylfumarate (5 mmoles) were dissolved in 20 ml of xylene and refluxed for a few days (Table 8). The cycloadducts 4 or 5 crystallized after removing the solvent. Two isomers 5a and 5b were obtained from 3 (X = Cl; R = CH_2Ph) and dimethylfumarate. They were separated by preparative TLC on silicagel using Et_2O–Ligroin (2:3) as the developing solvent.

Thermal stability of 4 and 5. The cycloadducts 4, 5a and 5b were kinetic products because they were recovered unchanged after being refluxed in xylene for the same time as for their preparation. However, when 4, 5a or 5b was heated at about 250°C (oil bath) for 0.5 hr, a retrocycloaddition was observed and the starting 3 and

Table 5. Bond lengths (Å) and angles (°) for nonhydrogen atoms, with esd's in parentheses

S–C(3)	1.833(6)	C(3)–S–C(6)	80.8(3)
S–C(6)	1.835(6)		
N–C(2)	1.367(7)	C(2)–N–C(6)	110.7(5)
C(2)–C(3)	1.549(9)	C(2)–N–C(11)	121.4(5)
C(3)–C(4)	1.565(9)	C(6)–N–C(11)	122.3(5)
C(4)–C(5)	1.581(8)		
C(5)–C(6)	1.55.(10)	N–C(2)–C(3)	108.1(5)
C(6)–N	1.489(8)	N–C(2)–0(2)	126.3(6)
		C(3)–C(2)–0(2)	125.6(5)
N–C(11)	1.445(8)		
C(2)–0(2)	1.200(8)	C(2)–C(3)–C(4)	105.0(5)
C(3)–C(31)	1.495(8)	C(2)–C(3)–C(31)	113.7(5)
C(4)–C(41)	1.523(10)	C(4)–C(3)–C(31)	115.9(5)
C(5)–C(51)	1.514(10)	C(2)–C(3)–S	100.3(4)
C(6)–C(61)	1.520(8)	C(4)–C(3)–S	102.5(4)
		C(31)–C(3)–S	117.4(5)
		C(3)–C(4)–C(5)	106.4(5)
		C(3)–C(4)–C(41)	111.2(5)
		C(5)–C(4)–C(41)	112.4(5)
		C(4)–C(5)–C(6)	103.2(5)
		C(4)–C(5)–C(51)	113.7(5)
		C(6)–C(5)–C(51)	113.4(5)
		C(5)–C(6)–N	106.1(5)
		C(5)–C(6)–C(61)	117.7(5)
		N–C(6)–C(61)	111.9(5)
		C(5)–C(6)–S	104.1(4)
		N–C(6)–S	102.0(4)
		C(61)–C(6)–S	113.5(5)
C(11)–C(12)	1.398(10)	C(16)–C(11)–C(12)	119.8(7)
C(12)–C(13)	1.385(15)	C(11)–C(12)–C(13)	119.2(8)
C(13)–C(14)	1.372(18)	C(12)–C(13)–C(14)	120.3(9)
C(14)–C(15)	1.379(16)	C(13)–C(14)–C(15)	120.7(10)
C(15)–C(16)	1.387(13)	C(14)–C(15)–C(16)	119.2(9)
C(16)–C(11)	1.372(11)	C(15)–C(16)–C(11)	120.7(8)
		N–C(11)–C(12)	120.5(7)
		N–C(11)–C(16)	119.7(6)
C(31)–C(32)	1.367(9)	C(36)–C(31)–C(32)	118.7(5)
C(32)–C(33)	1.388(8)	C(31)–C(32)–C(33)	121.6(6)
C(33)–C(34)	1.380(10)	C(32)–C(33)–C(34)	118.2(6)
C(34)–C(35)	1.373(11)	C(33)–C(34)–C(35)	121.7(6)
C(35)–C(36)	1.378(9)	C(34)–C(35)–C(36)	118.9(6)
C(36)–C(31)	1.395(9)	C(35)–C(36)–C(31)	120.8(6)
		C(3)–C(31)–C(32)	122.0(6)
		C(3)–C(31)–C(36)	119.3(6)
C(34)–C1	1.748(6)	C1–C(34)–C(33)	118.7(6)
		C1–C(34)–C(35)	119.5(5)
C(61)–C(62)	1.384(10)	C(66)–C(61)–C(62)	119.6(6)
C(62)–C(63)	1.386(9)	C(61)–C(62)–C(63)	119.7(6)
C(63)–C(64)	1.379(12)	C(62)–C(63)–C(64)	120.5(8)
C(64)–C(65)	1.367(12)	C(63)–C(64)–C(65)	120.1(7)
C(65)–C(66)	1.392(10)	C(64)–C(65)–C(66)	120.3(7)
C(66)–C(61)	1.393(9)	C(65)–C(66)–C(61)	119.8(7)
		C(6)–C(61)–C(62)	120.1(6)
		C(6)–C(61)–C(66)	120.0(6)
C(41)–0(41)	1.195(8)	C(4)–C(41)–0(41)	126.5(6)
C(41)–0(42)	1.329(9)	C(4)–C(41)–0(42)	108.4(6)
0(42)–C(42)	1.453(11)	0(41)–C(41)–0(42)	125.1(6)
		C(41)–0(42)–C(42)	115.5(6)
C(51)–0(51)	1.196(9)	C(5)–C(51)–0(51)	126.3(6)
C(51)–0(52)	1.330(8)	C(5)–C(51)–0(52)	109.9(6)
0(52)–C(52)	1.456(10)	0(51)–C(51)–0(52)	123.6(6)
		C(51)–0(52)–C(52)	116.5(6)

olefin were identified (IR, RMN, TLC). It is of interest to notice that the same retrocycloaddition was observed in the mass spectra of 4 and 5. This result is similar to the retro Diels–Alder fragmentations already described.[7]

Treatment of 4 *with sodium methoxide.* The reaction was carried on as in reference 3. The *cis* diester (0.5 mmole) in MeOH (30 ml) was treated with NaOMe (23 mg Na in 10 ml of MeOH). Quenching the reaction after 5 min with water deposited a solid which was identical in every aspect with the *trans* 5a. The filtrate gave 6 identical with an authentic sample prepared by the reaction of 3 and dimethylacetylene dicarboxylate.[4]

X-ray crystallography of 4 (X = Cl, R = Ph). A crystal of the cycloadduct in the form of a plate with the size of 0.17 × 0.15 × 0.07 mm was used for structure determination. The unit-cell parameters, given in Table 1, were determined from a least-squares refinement of the angular settings of 30 reflections carefully centered on an Enraf–Nonius CAD-4 diffractometer with Ni-filtered CuK_α radiation. The intensities were collected by the ω–2θ scan technique. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 10° to 2° min^{-1}. Background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan widths were determined by the equation,

$$\text{scan range} = A + B \tan \theta$$

where A = 0.6° and B = 0.2°. Aperture settings were determined in a like manner with A = 2.4 mm and B = 0.9 mm. As a check on the stability of the diffractometer and the crystal, three reflections were measured for intensity control at intervals of 100 reflections and six reflections were used for orientation controls after each 100th reflections.

An independent set of data was measured out to $\theta = 75°$, a total of 4992 unique reflexions were collected. As the crystal was small, many reflections were unobserved. Using a treshold value of 3σ (I) from counting statistics only 1240 reflections were observed. In order to obtain a better ratio of number of observations to number of variables (317) we used 1.5σ (I) and 2558 reflections were classified as observed and were included in the refinement. The intensities were corrected for Lorentz and polarization effects, but not for absorption (R ~ 0.25).

The structure was solved by direct methods using MULTAN 74.[8] E-map with the highest unit-weighted combined figure of merit revealed the locations of almost all non H-atoms. Additional $|F_o|$-Fourier-map completed the structure with all nonhydrogen atoms. Refinement was done by full-matrix least-squares with empirically determined weighting function of the form

$$W = W_F \times W_S$$

$$\begin{array}{lll} \text{where} & W_F = (|F_o|/23)^{2.0} & \text{if } |F_o| < 23 \\ & W_F = (45/|F_o|)^{1.5} & \text{if } |F_o| > 45 \\ \text{else} & W_F = 1.0 & \text{if } 23 < |F_o| < 45 \\ \text{and} & W_S = (\sin\theta/0.40)^{2.0} & \text{if } \sin\theta < 0.40 \\ & W_S = (0.75/\sin\theta)^{2.0} & \text{if } \sin\theta > 0.75 \\ & W_S = 1.0 & \text{if } 0.40 < \sin\theta < 0.75. \end{array}$$

Methylhydrogen atoms were located by a difference Fourier map and added to structure factors calculations at calculated positions as well as ring H-atoms at C–H distance of 1.06 Å and with isotropic temperature factors of B = 3.2 Å^2 but not refined. Neutral atom scattering factors were taken from compilation of Cromer and Mann,[9] for H-atoms those of Stewart *et al.*[10] Extinction and anomalous dispersion corrections for all nonhydrogen atoms with the data of Cromer and Liberman[11] were included. All the calculations were performed on the CDC Cyber 72 computer at RRC Ljubljana with the X RAY-72 system of crystallographic programs,[12] illustrations were obtained with the ORTEP.[13]

A final difference Fourier map showed no feature greater than 0.25 eÅ^{-3}. No systematic variation of $w(|F_o| - |F_c|)^2$ vs $|F_o|$ or $(\sin\theta)/\lambda$ was observed. The maximum and average shift-to-error ratios in the final cycle were 0.25 and 0.06. The agreement factors R and R_w are 0.092 and 0.077 for 2558 reflections. Including only 1240 reflections with I > 3σ (I) the analogous values are 0.039 and 0.045.

Table 6. Least-squares planes and dihedral angles x, y, z are fractional coordinates

Plane	Atom	Deviation (Å)	Equation to the plane
(a) Planes			
P1	S	0.0	$-9.265x - 1.892y + 15.27z = 0.0947$
	C(3)	0.0	
	C(6)	0.0	
P2	N	−0.013	$-6.700x + 7.100y + 11.14z = 2.681$
	C(2)	0.013	
	C(3)	−0.007	
	C(6)	0.008	
P3	C(3)	0.004	$3.583x + 9.410y - 5.557z = 2.697$
	C(4)	−0.006	
	C(5)	0.006	
	C(6)	−0.004	
P4	C(4)	0.000	$5.249x - 5.171y + 13.09z = 3.577$
	C(41)	−0.001	
	O(41)	0.000	
	O(42)	0.000	
P5	C(5)	−0.005	$11.06x - 1.492y + 2.622z = 3.459$
	C(51)	0.019	
	O(51)	−0.008	
	O(52)	−0.006	
P6	C(11)	0.000	$-2.804x - 2.157y + 20.21z = 3.484$
	C(12)	0.005	
	C(13)	−0.003	
	C(14)	−0.004	
	C(15)	0.008	
	C(16)	−0.007	
P7	C(31)	−0.020	$-8.214x - 4.311y + 14.64z = -0.331$
	C(32)	0.007	
	C(33)	0.012	
	C(34)	−0.019	
	C(35)	0.006	
	C(36)	0.013	
P8	C(61)	−0.012	$-6.655x - 7.173y + 10.98z = -1.815$
	C(62)	0.006	
	C(63)	0.002	
	C(64)	−0.004	
	C(65)	−0.002	
	C(66)	0.010	

(b) Dihedral angles (°)

	P1	P2	P3	P4	P5	P6	P7
P2	55.3						
P3	57.5	67.2					
P4	79.4	73.1	60.3				
P5	59.0	60.4	85.5	43.3			
P6	38.1	66.7	61.9	45.4	83.3		
P7	14.7	69.7	43.2	70.4	66.4	36.4	
P8	34.3	89.6	23.2	64.8	73.4	46.5	20.0

Table 7. IR and NMR spectra of the cycloadducts 4 and 5

Compounds	X	R	IR(CCl_4) νCO	δ_{OCH_3}[3]	NMR($CDCl_3$) δ_{CH_2Ph}	δH_4 and δH_5	JH_4H_5
4†	H	Ph	1767; 1751; 1721	3.34 3.45	—	4.42 (2)§	9.5
4	Cl	Ph	1767; 1750; 1719	3.38 3.48	—	4.40 (2)§	10
4	Cl	CH_2Ph	1764; 1750; 1707	3.34 3.46	4.29(s)(2)	3.86(d)(1) 4.45(d)(1)	13
5a‡	H	Ph	1740; 1718	3.47 3.70	—	4.28(d)(1) 4.51(d)(1)	4.5
5a	Cl	Ph	1741; 1716	 3.68		4.24(d)(1) 4.52(d)(1)	4.5
5a	Cl	CH_2Ph	1741; 1708	3.57 3.72	4.29(2)§ (J = 16Hz)	4.20 (2)§	4.5
5b	Cl	CH_2Ph	1743; 1709	3.35 3.80	3.77(d)(1) 4.85(d)(1) J = 15Hz	3.82(d)(1) 4.65(d)(1)	5

†This compound has the same melting point and the same spectra as reported for the cycloadduct described with endo ester groups.[3]
‡This compound has the same melting point and the same spectra as reported for the cycloadduct described under the structure **5b**.[3]
§AB quartet.

Table 8. Préparation of the cycloadducts 4 and 5

Compounds	X	R	boiling xylene t(h)	Yield	m.p.	Mass Spectra M^{+} calc.	found
4	H	Ph	120	93	218†	473.129685	473.1299
4	Cl	Ph	70	80	270	507.090713	507.0905
4	Cl	$PhCH_2$	137	92	250	521.106362	521.1054
5a	H	Ph	50	85	152‡	—	—
5a	Cl	Ph	70	80	184	507.090713	507.0905
5a	Cl	CH_2Ph	70	89	125	521.106362	521.1054
5b	Cl	CH_2Ph			178	521.106362	521.1054

†Litt. 215–216(3)
‡Litt. 151–152(3)

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