Rotamers and Isomers in the Fulgide Series. Part 2.† Stereochemistry and Conformational Analysis of Bis-(*p*-methoxybenzylidene)succinic Anhydrides by *X*-Ray Crystallography and Molecular Mechanics

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Crystalline bis-(*p*-methoxybenzylidene)succinic anhydrides occur as the methoxy rotamers of both *E,E* and *Z,Z* geometrical isomers. Three of these forms have been synthesized and characterized crystallographically while a fourth was simulated by force-field methods. Only one methoxy rotamer, the unsymmetrical variety of the *Z,Z* series, was observed, but two rotamers of the *E,E* form were obtained. A third possible *E,E* rotamer, not obtained experimentally, but predicted by molecular mechanics conformational analysis, is also described. The number of possible rotamers is restricted by the tendency of methoxy groups to be coplanar with the associated phenyl rings. Additional forms of the *E,E* series appear because of chirality introduced by steric repulsion between the superimposed phenyl rings.

The bis-(*p*-methoxybenzylidene)succinic anhydride obtained from the corresponding diacid synthesized *via* the Stobbe condensation[1] has been shown to be the *E,E*-isomer (**1**) by *X*-ray diffraction analysis.[2] It was reported[2] to be isomerized by irradiation at 366 nm to both the *E,Z*-isomer (**2**) and the *Z,Z*-isomer (**3**) which were separated by fractional crystallization.[2] These isomers were converted into the open-chain diacids which were not specifically distinguished from each other but which were dehydrated to re-form the starting anhydrides. The electronic absorption reported for the *Z,Z*-isomer showed a very strong peak at *ca.* 420 nm (ε *ca.* 40 000 from the figure shown).[2] The n.m.r. values reported for the *E,E*-isomer (**1**) and the *Z,Z*-isomer (**3**) were unusual in that the olefinic protons were reported as having identical resonances (at δ 7.87), whereas it has recently been confirmed[3] that in the symmetrical fulgide series the olefinic protons are clearly different in *E,E*- as against *Z,Z*-structures due to the different magnetic effects of the neighbouring carbonyl groups upon them.[3] The *E,Z*-anhydride (**2**) has been separately listed[3] but the published details[4] of its preparation could not be made available to us.

We prepared the *E,E*-anhydride (**1**) and our data are in agreement with earlier reports.[1,2] This isomer, deep yellow prisms, m.p. 168—168.5 °C, has the two methoxy groups oriented in the same sense (**4**), as also shown before.[2] We were able to confirm this directional characteristic for our preparation also. On heating the solution in acetone, however, we obtained a rotamer of it as orange prisms, m.p. 176—176.5 °C. *X*-Ray diffraction analysis showed that in this case the two methoxy groups are oriented in opposed senses (**5**). The close proximity of the two aromatic rings in these structures thus leads to a sufficiently high energy barrier to restrict rotation of the methoxy groups in these highly compressed systems in the solid state. In solution the two rotamers showed identical behaviour with respect to u.v. absorption and n.m.r. characteristics, so that rapid interconversion is demonstrated for the solvated state. The structure of a possible isomer (**6**), not observed in our experiment, was established by molecular mechanics simulation.

On irradiating a solution of (**1**) in acetone at 366 nm we obtained the *Z,Z*-anhydride (**3**). As here obtained, it occurred as red needles, m.p. 166—168 °C, whereas the previously reported[2] m.p. was 194—195 °C. We were not able to find any *E,Z*-isomer in the irradiation product (see Experimental section).

The u.v. absorption characteristics were as formerly described,[2] but the n.m.r. spectra differed for the olefinic proton resonance which we found at δ 7.33 as against the reported[2] value of δ 7.87. Crystals suitable for *X*-ray diffraction studies yielded the *Z,Z*-structure (**7**) with the methoxy groups disymmetrically arranged. All our n.m.r. spectra of this compound, however, show only one set of resonances so that the compound in solution would have a symmetrical arrangement of the substituents available [as, for instance, in (**8**)] and hence a two-fold axis of symmetry. This parallels the behaviour in solution here found for the *E,E*-isomers (**4**) and (**5**).

Identical *X*-ray powder diffraction patterns were obtained for the irradiation product crystallized once, and for the same preparation after four crystallizations.

The very intense absorption of the *Z,Z*-anhydride (**3**) (ε 40 000 at 420 nm) suggests an unusually strong interaction between the carbonyl groups and the adjacent aromatic rings in this configuration and this is being studied in a more general context.

Experimental

Measurements routinely involved Kofler micro hot-stage (m.p.), Unicam SP1800 (u.v.-visible), Varian-MAT (m.s.), Bruker WP 80 MHz Fourier transform spectrometer (n.m.r., in deuteriochloroform solutions), and Pye-Unicam (g.l.c.) instruments. T.l.c. was on pre-coated silica gel plates (Merck F254). Analytical g.l.c. of silylated acids was over a column (1.4 × 0.0016 m) of OV17 (1% on Anakrom Q) with nitrogen as carrier gas at 24 ml min^{-1}, runs were programmed at 8 °C min^{-1}, injector and detector ports were at 300 °C, and emergent peak temperatures (ET) were read from the oven thermometer. Approximate product distributions were calculated from measured peak heights.[5]

E,E-*Bis-*(p-*methoxybenzylidene*)*succinic Acid* (**9**).—This was obtained from anisaldehyde (2 mol) and diethyl succinate (1 mol) with sodium hydride[6] (2 mol) as yellow grains, m.p. 223—227 °C (decomp.) [lit., 242—243 °C (decomp.),[1] 202—203 °C[7]).

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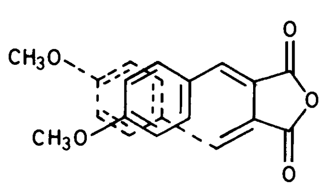
† Part 1, ref. 10.



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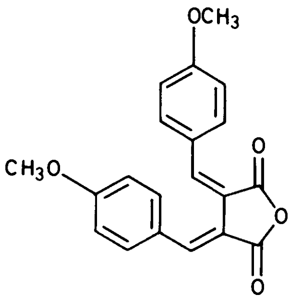

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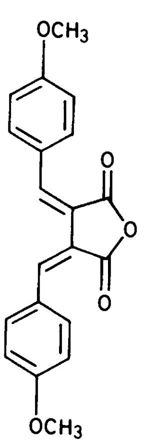

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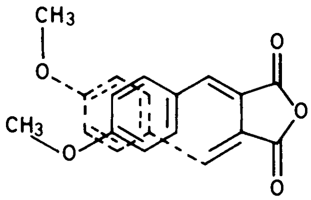

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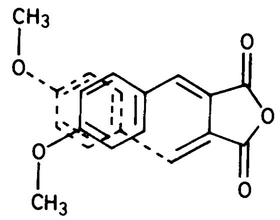

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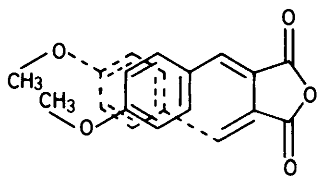

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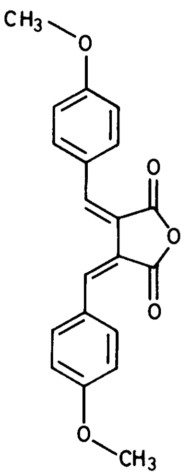

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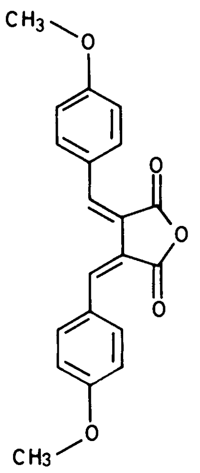

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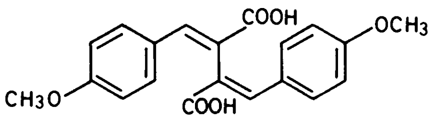

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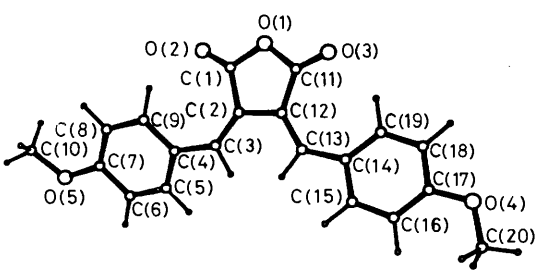

Figure 1. The crystallographic atomic numbering scheme. Hydrogen atoms are numbered by reference to the numbers of connected carbon atoms

Silylation analysis showed it to be 99% pure, with ET_{176} 254 °C (silyl ester: Found: M^+, 498.190. $C_{26}H_{34}O_6Si_2$ requires *M*, 498.189).

The corresponding E,E-*anhydride* (**1**) was obtained from the diacid with acetyl chloride [1,2] as deep yellow prisms, m.p. 168—168.5 °C from benzene [lit., 170—171 °C (from carbon disulphide),[1] 164—165 °C (from benzene)[2]]; *m/z* 336 (M^+, 100%); δ 7.86 (2 H, s, olefinic H), 6.74 (4 H, d, *J* 9 Hz, aromatic H), 6.41 (4 H, d, *J* 9 Hz, aromatic H), and 3.73 (6 H, s, OCH_3) as found previously;[2,3] $\lambda_{max.}$ (MeCN) 375 (br, ε 15 000), 315 (35 000), 255 (10 000), and 226 nm (15 000). These crystals were suitable for *X*-ray diffraction analysis and afforded the *E,E*-anhydride structure (**4**) with the two methoxy groups oriented in the same sense as found earlier. On boiling a solution of these crystals in acetone and then cooling, deeper coloured orange prisms and octahedra were formed of the rotamer (**5**), m.p. 176—176.5 °C (Found: *M*, 336.096. $C_{20}H_{16}O_5$ requires *M*, 336.100), *m/z* 336 (M^+, 100%) and u.v. (in acetonitrile solution) and n.m.r. characteristics identical with those of the crystals (**4**) with m.p. 168—168.5 °C.

The same higher-melting crystals were subsequently obtained by crystallization from benzene of the mother liquors of the crystallization from acetone. The crystals were suitable for *X*-

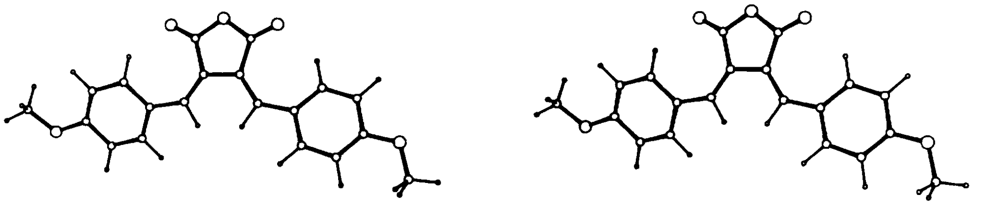

Figure 2. Stereoscopic view of the molecule of (7) in the crystal

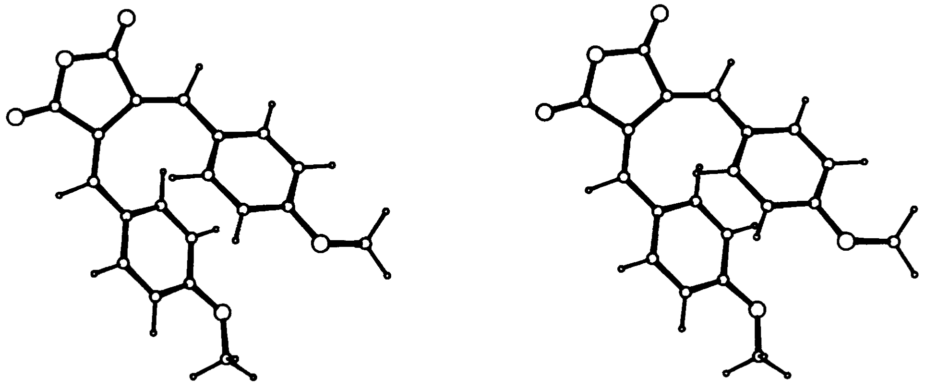

Figure 3. Stereoscopic view of the molecule of (5) in the crystal

Table 1. Crystal data and details of the crystallographic analysis of structures (7) and (5)

Compound	(7)	(5)
M_r	336.34	336.34
Space group	$P2_1/n$	$P2_1/a$
a/Å	4.648(1)	10.732(2)
b/Å	11.770(1)	18.984(3)
c/Å	29.506(3)	8.494(1)
β/°	91.19(2)	104.62(1)
V/Å^3	1 613.8	1 674.5
Z	4	4
D_c (g cm^{-3})	1.38	1.33
F(000)	704	704
Radiation	Cu-K_α	Mo-K_α
μ/cm^{-1}	7.32	0.57
Scan range (°)	$3.0 < \theta < 75.0$	$3.0 < \theta < 30.0$
Scan type	ω–2θ	ω–2θ
h	−5 to 5	0 to 15
k	0 to 14	0 to 26
l	0 to 36	−11 to 11
Number of data	2 756	3 971
Internal consistency, R	0.01	0.02
Number F_{obs}	1 898 > 3$\sigma(F)$	2 385 > 4$\sigma(F)$
Number of parameters	227	227
Maximum shift (σ)	0.02	0.001
Residual density		
Maximum (e Å^{-3})	0.2	0.2
Minimum (e Å^{-3})	−0.3	−0.3
R	0.06	0.05
Weighing scheme	unit	unit

ray diffraction and afforded the rotameric *E*,*E*-anhydride structure (5) with the methoxy groups oriented in opposed senses.

Z,*Z*-*Bis*-(p-*methoxybenzylidene*)*succinic Anhydride* (3).—The foregoing *E*,*E*-anhydride (4) (420 mg) in acetone solution (50 ml) was irradiated at 366 nm with a medium-pressure mercury lamp (Applied Photophysics model 3010; 125 W) in a water-cooled Pyrex well for 2 h, when by t.l.c. in benzene–ethyl acetate (19:1, v/v) the starting material with hR_F 37 had largely changed to a product with hR_F 47. Crystallization of the recovered product (421 mg) from acetonitrile gave red prismatic needles (244 mg) of the *Z*,*Z*-anhydride (3), m.p. 163—168 °C; *m*/*z* 336 (M^+, 100%); δ 8.11 (4 H, d, *J* 9 Hz, aromatic H), 7.33 (2 H, s, olefinic H), 6.97 (4 H, d, *J* 9 Hz, aromatic H), and 3.89 (6 H, s, OCH$_3$). *X*-Ray diffraction analysis of these crystals afforded the *Z*,*Z*-anhydride structure (7).

After three further crystallizations from acetonitrile the final material was red needles, m.p. 166—168 °C (Found: M^+, 336.099. $C_{20}H_{16}O_5$ requires *M*, 336.100); $\lambda_{max.}$(MeCN) 420 (ε 40 000) 327 (21 000), 255 (9 000), and 227 nm (11 000) as previously reported;[2] *m*/*z* 336 (M^+, 100%); and n.m.r. characteristics identical with those of the first batch of these crystals (above). The powder diffraction patterns for the two batches of crystals were also identical.

The mother liquors of these crystallizations were re-worked for further products. Crystallizations from benzene and then from acetonitrile gave red prisms (as above) mixed with clear yellow prisms. The latter were obtained pure by fractional crystallization from acetonitrile as clear yellow needles (70 mg) of unchanged *E*,*E*-anhydride (5), m.p. 174—175 °C (Found: M^+, 336.105. $C_{20}H_{16}O_5$ requires *M*, 336.100); *m*/*z* 336 (M^+, 100%) and the same fragmentation pattern as before; δ 7.86 (2 H, s), 6.73 (4 H, d, *J* 9 Hz), 6.40 (4 H, d, *J* 9 Hz), and 3.72 (6 H, s) as for the starting material. No other crystalline forms were encountered.

Crystal Structures.—The structures of (7) and (5), for comparison with the known[2] structure of (4), were determined by *X*-ray crystallography. Crystal quality was assessed by standard photographic techniques and although crystals of (7) were very small and fibrous, compared with those of (5), their diffraction pattern was satisfactory for structure analysis.

Accurate cell parameters were obtained from least-squares refinement of 25 high-order θ values, randomly sampled from

Table 2. Fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms of compound (**7**)

	x	y	z
O(1)	2 670(9)	8 326(3)	976(1)
O(2)	791(10)	9 178(4)	565(1)
O(3)	6 133(10)	7 856(4)	1 473(2)
O(4)	13 515(9)	9 675(3)	3 220(1)
O(5)	−7 276(9)	13 940(3)	196(1)
C(1)	1 045(13)	9 280(5)	854(2)
C(2)	1 956(11)	10 236(4)	1 142(2)
C(3)	809(11)	11 287(5)	1 157(2)
C(4)	−1 329(11)	11 892(4)	883(2)
C(5)	−2 495(11)	12 876(5)	1 072(2)
C(6)	−4 496(12)	13 526(5)	843(2)
C(7)	−5 351(11)	13 228(5)	405(2)
C(8)	−4 219(13)	12 265(5)	209(2)
C(9)	−2 224(12)	11 608(5)	445(2)
C(10)	−7 958(14)	13 745(5)	−280(2)
C(11)	4 567(12)	8 584(5)	1 330(2)
C(12)	4 197(11)	9 782(4)	1 454(2)
C(13)	5 626(11)	10 392(5)	1 776(2)
C(14)	7 755(11)	10 136(4)	2 133(2)
C(15)	8 863(12)	11 065(5)	2 367(2)
C(16)	10 825(12)	10 964(5)	2 726(2)
C(17)	11 675(11)	9 884(5)	2 861(2)
C(18)	10 633(12)	8 943(5)	2 631(2)
C(19)	8 699(12)	9 059(5)	2 270(2)
C(20)	14 524(15)	10 639(5)	3 487(2)

Table 3. Fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms of compound (**5**)

	x	y	z
O(1)	4 401(2)	8 276(1)	1 532(3)
O(2)	3 182(3)	7 418(2)	2 143(4)
O(3)	5 999(2)	8 899(1)	968(3)
O(4)	11 247(2)	5 560(1)	4 305(3)
O(5)	8 530(3)	4 391(1)	492(3)
C(1)	4 179(4)	7 575(2)	1 880(5)
C(2)	5 311(3)	7 151(2)	1 799(4)
C(3)	5 165(3)	6 442(2)	1 700(4)
C(4)	6002(3)	5 910(1)	1 334(3)
C(5)	6 862(3)	6 037(1)	372(3)
C(6)	7 670(4)	5 523(2)	89(3)
C(7)	7 658(4)	4 858(2)	806(4)
C(8)	6 795(4)	4 713(2)	1 723(4)
C(9)	5 961(3)	5 227(2)	1 958(4)
C(10)	8 667(5)	3 729(2)	1 300(5)
C(11)	5 642(3)	8 346(2)	1 335(3)
C(12)	6 305(3)	7 656(1)	1 683(3)
C(13)	7 601(3)	7 661(1)	1 988(3)
C(14)	8 542(2)	7 121(1)	2 618(3)
C(15)	8 323(3)	6 563(1)	3 612(3)
C(16)	9 244(3)	6 061(1)	4 166(3)
C(17)	10 406(3)	6 091(1)	3 724(3)
C(18)	10 663(3)	6 642(1)	2 770(3)
C(19)	9 739(3)	7 152(1)	2 250(3)
C(20)	12 425(3)	5 534(2)	3 819(4)

reciprocal space, and measured on an Enraf–Nonius CAD4 diffractometer, equipped with an incident-beam graphite-crystal monochromator, at room temperature. The same instrument was used for diffraction data collection according to the specifications of Table 1. Data reduction consisted of correction for background and L_p factors only. In the case of (**5**) it was necessary to allow for isotropic decay as suggested by a monotonic decrease in intensity of three standard reflections measured at regular intervals during data collection. The structures were solved by direct methods using the program[8] SHELXS86. All non-hydrogen atoms were located on the first *E* maps and despite the molecular two-fold axis of (**5**), both molecules were found in general position. The structures were refined by full-matrix least-squares, first isotropically and then anisotropically for the non-hydrogen atoms, using the program[9] SHELX76. Although a fair number could be located by difference synthesis, most of the hydrogen atoms were placed in geometrically calculated positions and refined in riding mode with a common isotropic temperature parameter. The atomic numbering scheme is defined in Figure 1 and the final fractional atomic co-ordinates are in Tables 2, for compound (**7**), and 3, for (**5**). Important molecular parameters are summarized and compared with (**4**) in Table 4. An interesting feature, also noticed before,[10] relates to the orientation of the methoxy groups relative to their phenyl rings. Not only are the methoxy groups approximately coplanar with the rings, but the connecting bonds always tend to be directed away from the external bisector by *ca.* 6°. Anisotropic thermal vibration parameters and hydrogen fractional co-ordinates and bond lengths and angles have been deposited in the Cambridge Crystallographic Data Centre. Stereoscopic drawings of the molecular structures of (**5**) and (**7**) as found crystallographically are shown in Figures 3 and 2. Stereoscopic packing diagrams are shown in Figures 4 and 5.

The only significant differences between the two structures substantiated by the data are the conformation of the five-membered ring. This relates to the essential planarity of the *cis* structure of the *Z*,*Z*-isomer (**7**), compared with the sterically strained situation introducted by the overcrowded *trans* arrangement of phenyl rings in the symmetrical *E*,*E*-isomer (**5**). The strain puckers the anhydride ring into a symmetrical $^3T_4$ conformation[10] and bends the double bonds outwards from an almost bisecting position in the *Z*,*Z*-structure. The same distortion is found in the unsymmetrical *Z*,*Z*-rotameric structure (**4**), published before.[2]

The only common crystalline rotamer characterized in this and in previous work[2] is compound (**4**). This could be due to a remarkable sensitivity of crystal type for solvent effects, although no solvates appear to be formed. Apart from the three forms (**4**), (**5**), and (**7**) now characterized, a third variety of the *E*,*E*-isomer (from acetone–light petroleum) and two other varieties of *Z*,*Z* (from acetonitrile and acetone respectively) were isolated before[2] and characterized in terms of unit cells and space groups. Compared to the calculated densities of 1.33 and 1.35 g cm^{-3} of (**5**) and (**4**) respectively, the unidentified *E*,*E*-rotamer is described[2] with a density of 1.57 g cm^{-3}. The two additional *Z*,*Z*-rotamers have calculated densities of 1.70 and 1.39 g cm^{-3}, compared with 1.38 g cm^{-3} of (**7**). In addition, there is a *cis-trans* form of density 1.33 g cm^{-3}. The surprising result[2] concerns the two crystals of anomalously high density. It is reasonable that the *Z*,*Z* forms should be of higher density ($\pm$1.38 g cm^{-3}) than the *E*,*E* forms ($\pm$1.34 g cm^{-3}). However, the reported[2] densities of 1.70 and 1.57 g cm^{-3} cannot be rationalized. All efforts to reproduce previous results[2] by recrystallization from specified solvents failed.

Molecular Mechanics.—The crystallographic analyses of bis-(*p*-methoxybenzylidene)succinic anhydrides suggest that rotational isomerism could arise from rotation of either methoxyphenyl groups or methoxy groups, in addition to geometrical isomerism at the double bonds. Rotation of methoxyphenyl groups has been analysed elsewhere[11] for dimethoxyphenyls, where rotamerism of simple methoxy groups does not occur. The latter will now be considered.

For a given configuration of phenyl groups, possible methoxy rotamers should be predictable from an analysis of a two-dimensional steric plot in terms of independent rotations around the two OCH_3 bonds. A suitable program which

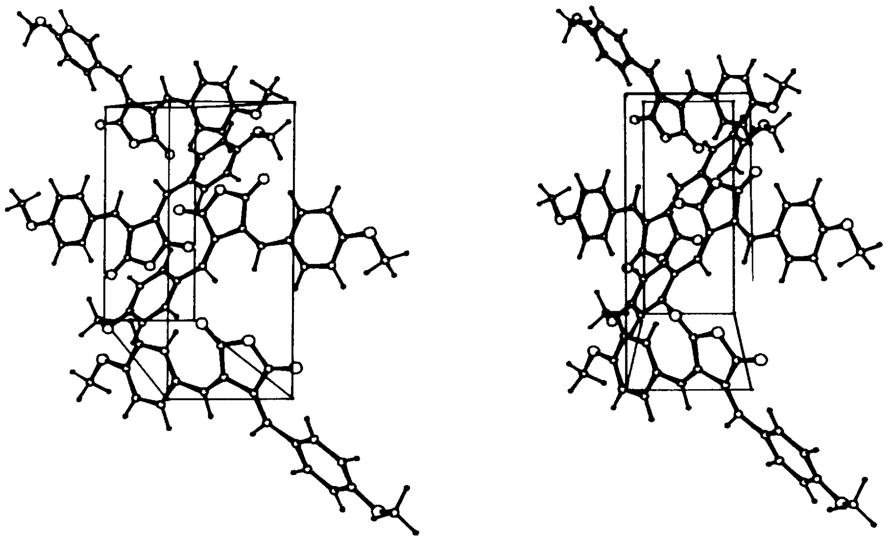

Figure 4. Stereoscopic packing diagram of (7)

Table 4. Important bonding parameters observed in the structures of (**7**) and (**5**) in comparison with literature results,[2] and averaged over chemically equivalent entities. Bond lengths are in Å and all angles in degrees

Parameter	(7)	(5)	(4) Literature (Estimated mean σ = 0.008 Å and 0.54°)
O(1)–C(1)	1.391(4)	1.393(2)	1.378
C(1)=O(2)	1.198(4)	1.186(2)	1.178
C(1)–C(2)	1.468(5)	1.479(3)	1.514
C(2)=C(12)	1.476(6)	1.457(4)	1.417
C(2)–C(3)	1.351(5)	1.352(2)	1.355
C(3)–C(4)	1.459(5)	1.440(2)	1.461
C(7)–O(5)	1.367(4)	1.362(2)	1.376
O(5)–C(10)	1.452(5)	1.424(2)	1.463
C(1)–O(1)–C(11)	110.6(4)	109.7(2)	110.9
O(1)–C(1)–C(2)	108.7(3)	108.7(2)	108.1
O(1)–C(1)–O(2)	118.7(4)	119.7(2)	122.0
O(2)–C(1)–C(2)	132.7(4)	131.7(2)	130.0
C(1)–C(2)–C(12)	106.0(3)	105.7(2)	106.2
C(1)–C(2)=C(3)	128.3(3)	117.2(2)	115.7
C(3)=C(2)–C(12)	125.5(4)	136.7(2)	137.8
C(2)=C(3)–C(4)	134.3(4)	130.6(2)	129.5
C(8)–C(7)–O(5)*	124.3(4)	124.3(2)	124.8
C(6)–C(7)–O(5)†	116.1(4)	115.2(2)	113.2
C(7)–O(5)–C(10)	117.9(3)	118.3(2)	117.2
C(1)–O(1)–C(11)–C(12)	0.4(7)	−4.0(3)	
O(1)–C(1)–C(2)–C(12)	−1.2(7)	10.3(3)	
C(1)–C(2)–C(12)–C(11)	1.4(9)	−12.1(4)	
C(1)–C(2)=C(3)–C(4)	−7.6(8)		
C(12)–C(2)=C(3)–C(4)		−2.5(5)	
C(2)=C(3)–C(4)–C(9)	−13.4(8)		
C(2)=C(3)–C(4)–C(5)		−26.5	
C(8)–C)7)–O(5)–C(10)	2(1)	−5.9(4)	

* Average over outside angles. † Average over inside angles.

minimizes steric energy after each rotational step was described before[11] and the force-field previously adapted for dimethoxy fulgides[10] was used. The two relevant torsion angles were both driven through 360° in 20° steps. The starting co-ordinates for the analysis of *E,E* forms were obtained by orthogonalizing the fractional atomic co-ordinates from the crystal structure of (**5**). The resulting conformational map of steric energy is shown in Figure 6. Energy minima occur at (φ_1,φ_2) = (0,0), (0, ± 90), (0,180), (180, ± 90), and (180,180)°, predicting four planar and four non-planar rotamers, differing by <4 kJ mol^{-1} in steric energy. The fact that only planar or near-planar forms are found experimentally suggests that some electronic factor is the cause of this preferred configuration, as previously suggested[12] by reference to conjugation between the substituent *p*-type lone pairs and the aromatic system. If, on this basis the perpendicular arrangements are discounted, four possible *E,E* rotamers are predicted, but these are not all independent. The forms (0,180) and (180,0) are in fact identical and the only possible rotamers are (0,0), (0,180), and (180,180). The first of these is described here (**5**) and the second was observed by Cohen[2] and confirmed by the present work. The third form could conceivably represent one of the unidentified products observed before[2] but no experimental verification can be offered. The most likely structure of the third rotamer, obtained by molecular mechanics, is shown in Figure 7. Cartesian atomic co-ordinates of the calculated structure are given in Table 5.

Discussion

The possible products of ring closure in bis-(*p*-methoxybenzylidene)succinic acid to form anhydrides depend on the relative rotational freedom about the three bonds marked α, β, and δ in the molecular diagram. The conformational analysis is complicated by the low barrier to rotation of the methoxy groups around the bonds marked δ. Cohen and his collaborators[2] characterized one of the products (**4**) crystallographically and two further crystalline isomers are described in this paper (**5**) and (**7**).

The observed bond parameters agree well with accepted literature values.[2,13] The packing diagrams are shown in Figures 4 and 5, respectively.

The most interesting feature to emerge from the structure determination of (**7**) is the unexpected conformation rather than one of the possible symmetrical forms, like (**8**). Furthermore the two aryl rings do not have the same orientation with respect to the anhydride ring, but this is compatible with the open structure and the relative freedom of rotation of the methoxy groups.

The observed structure of (**5**) completes a remarkable observation, together, with the previous characterization[2] of rotamer (**4**). To our knowledge, this is the first authentic separation of rotamers arising from reorientation of a simple

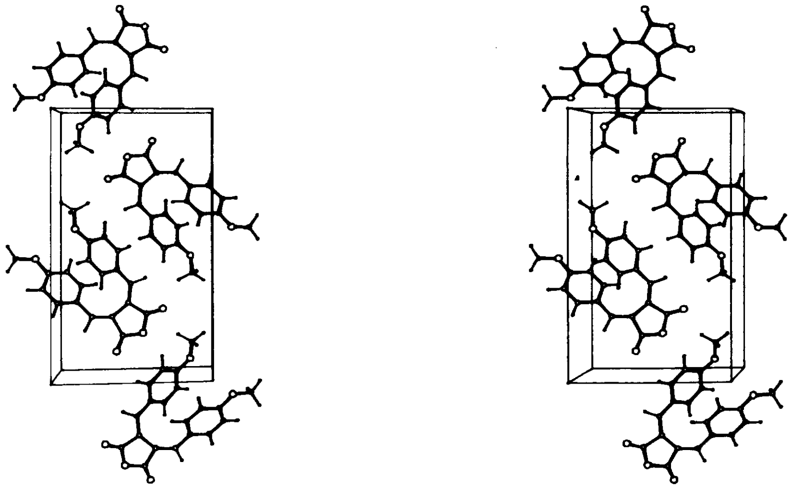

Figure 5. Stereoscopic packing diagram of (5)

Table 5. Calculated orthogonalized co-ordinates for compound (6)

O(1)	6.554 18	9.586 54	3.358 80
O(2)	8.397 77	9.240 34	4.656 64
O(3)	4.870 27	9.234 86	1.856 44
O(4)	5.672 95	1.191 55	5.717 43
O(5)	6.694 11	0.913 17	1.803 92
C(1)	7.473 21	8.784 09	4.050 72
C(2)	7.037 21	7.374 89	3.932 15
C(3)	7.558 00	6.430 69	4.767 01
C(4)	7.006 94	5.123 46	5.110 81
C(5)	7.885 52	4.119 27	5.551 52
C(6)	7.422 34	2.809 45	5.752 49
C(7)	6.070 27	2.484 81	5.530 24
C(8)	5.182 87	3.503 39	5.129 48
C(9)	5.647 66	4.812 03	4.927 77
C(10)	4.372 56	0.746 52	5.291 27
C(11)	5.661 78	8.781 90	2.633 63
C(12)	5.922 57	7.368 35	2.988 54
C(13)	5.332 89	6.377 83	2.259 82
C(14)	5.748 82	4.993 36	2.055 02
C(15)	4.774 67	4.047 92	1.688 99
C(16)	5.105 53	2.686 87	1.599 97
C(17)	6.414 85	2.248 00	1.877 72
C(18)	7.396 51	3.199 58	2.220 45
C(19)	7.065 88	4.561 22	2.300 70
C(20)	7.957 06	0.376 61	2.240 61
H(3)	8.276 32	6.784 46	5.489 28
H(5)	8.936 82	4.335 34	5.683 77
H(6)	8.120 62	2.041 71	6.058 19
H(8)	4.135 73	3.297 55	4.958 44
H(9)	4.947 66	5.564 92	4.600 55
H(101)	4.180 45	−0.306 85	5.445 88
H(102)	3.535 72	1.224 14	5.785 50
H(103)	4.164 58	0.883 47	4.236 98
H(13)	4.693 84	6.681 49	1.445 74
H(15)	3.751 78	4.357 27	1.516 81
H(16)	4.336 53	1.971 50	1.338 66
H(18)	8.414 35	2.902 79	2.435 98
H(19)	7.835 70	5.264 58	2.578 69
H(201)	8.044 89	−0.698 28	2.158 79
H(202)	8.821 83	0.736 27	1.699 76
H(203)	8.201 61	0.569 89	3.277 10

group such as methoxy. The increased barrier to rotation of the methoxy group, brought about by the increased steric demand of the eclipsed aryl rings, appears to be sufficient to ensure resolution of rotamers. Steger[14] recently reported a variable-

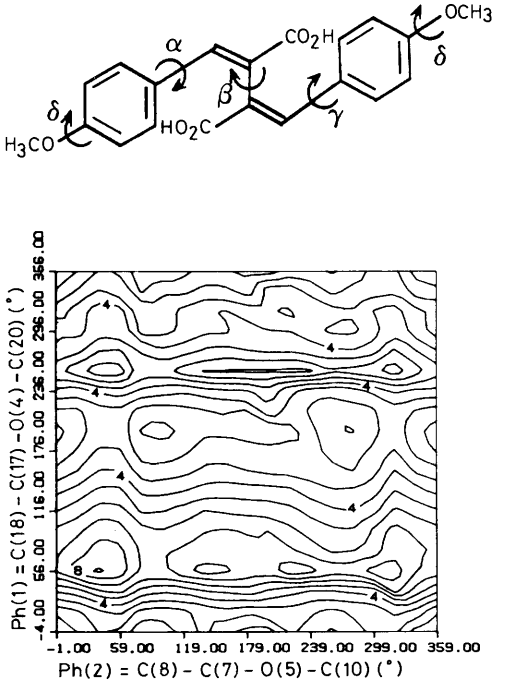

Figure 6. Molecular mechanics potential energy surface corresponding to rotation of the two methoxy groups of the *E*,*E*-isomer

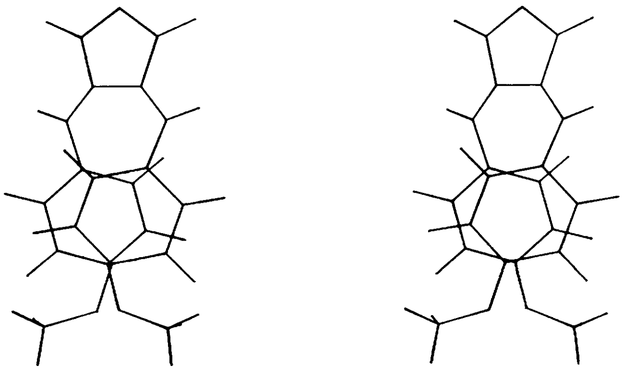

Figure 7. Energy-minimized structure of an unobserved rotamer of (5) obtained by molecular mechanics simulation

temperature n.m.r. study of the steric interaction in *E*,*E*-bis-(*p*-methoxybenzylidene)succinic anhydride in deuteriated acetone over the temperature range of 28 to −90 °C. The internal rotation of the δ methoxy groups was found to be frozen at −90 °C. A barrier height of 10.04 kcal mol^{-1} was calculated using the coalescence method.

The calculated barrier height (Figure 6) is less than the experimental value because no provision was made for the interaction between methoxy groups and aromatic π-systems. This would remove the sub-minima at (90,90)° and equivalent positions to raise the barrier between the remaining sub-minima substantially.

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