On the Crystal Structures of Two Diels-Alder Dimers, Formed upon Oxidation of *o*-Vanillin and Isovanillin by Thallium(III) Nitrate

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The crystal structures of 2,8-bis-(dimethoxymethyl)-5,5,9,9-tetramethoxy-1,4a,5,8a-tetrahydro-1,4-ethanonaphthalene-6,10(4*H*)-dione (=*A*) and 1,7-bis-(dimethoxymethyl)-5,5,9,9-tetramethoxy-1,4a,5,8a-tetrahydro-1,4-ethanonaphthalene-6,10(4*H*)-dione (=*B*) were solved by the direct method. Refinements, based on X-ray diffractometer data, were carried out by the full-matrix least-squares method to final values of $R = 0.088$ for 3249 reflexions (*A*) and $R = 0.039$ for 2343 reflexions (*B*). Both compounds crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$. The respective unit cells are of dimensions $a = 9.174$, $b = 10.179$, $c = 14.539$ Å, $\alpha = 97.64$, $\beta = 96.80$, $\gamma = 116.90°$ (*A*) and $a = 16.332$, $b = 6.836$, $c = 10.660$ Å, $\alpha = 96.56$, $\beta = 93.58$, $\gamma = 104.77°$ (*B*).

Compound *A* is formed upon oxidation of isovanillin by thallium(III) nitrate in methanol at 0 °C and *B* by the corresponding oxidation of *o*-vanillin.

The stereostructure of the dimerization products is in consonance with the *endo* rule. The structures are rather strained, having long C(*sp²*) — C(*sp³*) and C(*sp³*) — C(*sp³*) bonds. A disordered dimethoxymethyl group is observed in *A*.

Phenols, substituted with electron-donating groups in the *para* position, can be smoothly oxidized by thallium(III) nitrate to yield *p*-quinols.[1] Analogously, the oxidation of isovanillin and *o*-vanillin by this reagent at 0 °C in methanol yields,[2] with concomitant acetalization of the aldehyde function, 6,6-dimethoxy-3-dimethoxymethyl-2,4-cyclohexadien-1-one and 6,6-dimethoxy-2-dimethoxymethyl-2,4-cyclohexadien-1-one, respectively. These initially formed monomers, however, cannot be isolated in a pure state, as they spontaneously dimerize

in Diels-Alder cycloaddition reactions to yield 2,8-bis-(dimethoxymethyl)-5,5,9,9-tetramethoxy-1,4a,5,8a-tetrahydro-1,4-ethanonaphthalene-6,10(4*H*)-dione and 1,7-bis-(dimethoxymethyl)-5,5,9,9-tetramethoxy-1,4a,5,8a-tetrahydro-1,4-ethanonaphthalene-6,10(4*H*)-dione, henceforth called *A* and *B*, respectively. Only one of the many conceivable isomers was formed in the respective dimerization reaction.

Crystals of both compounds were prepared by Antus and Nógrádi. The structure of dimers have been established by NMR spectroscopy (SA & MN). X-Ray analysis (BK & AMP), however, was needed to settle the ambiguity of *endo* or *exo* stereostructure of the compounds.

Table 1. Crystal data. Cell dimensions were determined from least-squares treatment of the angular positions of 25 accurately centered reflexions on a Philips PW 1100 diffractometer. Estimated standard deviations are given within parentheses.

	A	*B*
a (Å)	9.174(2)	16.332(2)
b (Å)	10.179(2)	6.836(2)
c (Å)	14.539(3)	10.660(1)
α (°)	97.64(1)	96.56(1)
β (°)	96.80(1)	93.58(1)
γ (°)	116.90(1)	104.77(1)
V (Å³)	1175	1138
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_{X-ray} (g cm⁻³)	1.29	1.33
μ(CuKα) (cm⁻¹)	8.67	8.95

Table 2. Pertinent information about data collection, and structure elucidation and refinement for A and B.

Item	A	B
X-Radiation for the data collection Scan method	CuKα (graphite monochromated) θ-2θ scan, rate 1.2° (θ) min⁻¹, scan width 1.5° (θ). Backgrounds were estimated by stationary measurements.	CuKα (graphite monochromated) θ-2θ scan, rate 1.8° (θ) min⁻¹, scan width 1.5° (θ). Backgrounds were estimated by stationary measurements.
Number of unique reflexions recorded	$3989, \theta_{max} = 65°$	$3389, \theta_{max} = 60°$
Number of reflexions used in refinements	$3249, I_{net} \geq 4\sigma(I_{net})$	$2343, I_{net} \geq 4\sigma(I_{net})$
Standard reflexions	3 measured every hour.	3 measured every hour.
Behavior of standard reflexions	A linear decrease of the intensity of approx. 4 % over a period of 8 days.	No significant variation.
Reduction to structure factors	Lp-corrections; no correction for absorption.	Lp-corrections; no correction for absorption.
Structure determination	Initial structure (27 atoms) from MULTAN [3] (200 |E|'s ≥ 1.97, 634 unique phase relationships). Remaining 5 non-hydrogens from a difference F map.* H not looked for.	Initial structure (29 atoms) from MULTAN [3] (200 |E|'s ≥ 1.90, 728 unique phase relationships). Remaining 3 non-hydrogens from a difference F map. H from difference F map and chemical reasoning.
Refinement	Full-matrix least-squares based on F. C and O refined with anisotropic temperature factors. Some atoms refined with occupancy factors.* Hughes' weighting scheme. [4] 17 refl. were given zero-weight in the final cycles.	Full-matrix least-squares based on F. C and O included with anisotropic temperature factors; H included with fixed isotropic temperature factors. Hughes' weighting scheme. [4] 4 refl. were given zero-weight in the final cycles.
Atomic scattering factors	From the International Tables for X-Ray Crystallography. [5]	From the International Tables for X-Ray Crystallography. [5]
Final R value excl. n zero-weight refl.	0.088*, $n=17$	0.039, $n=4$

* The R-value converged to 0.125, but not further. A difference F synthesis computed at this stage showed one predominant peak, corresponding to approximately three electrons in the "center" of the dimethoxymethyl group consisting of the atoms C(11)−C(15), cf. Fig. 3a. Inclusion of occupancy factors for the atoms of this group and the "new atom", later labelled O(12)', reduced R to its final value of 0.088, and yielded occupancy factors of approximately 1 for all atoms except O(12) and O(12)', which adopted the values 0.6 and 0.4, respectively. Correlation coefficients show no significant coupling between occupancy factors and thermal parameters. A difference F synthesis at R=0.088 shows no peaks other than those corresponding to H atoms. No hydrogens, however, were included in the refinement.

X-RAY EXPERIMENTAL AND CRYSTAL DATA

Crystal data are summarized in Table 1. Standard methods were used for data collection and structure determination. Pertinent details are given in Table 2. Full-matrix least-squares refinement yielded final R values of 0.088 and 0.039 for A and B, respectively. The lower accuracy in the structural parameters obtained for A is an effect of a disordered dimethoxymethyl group — see footnote in Table 2 — and also of the fact that no hydrogen atoms were located in this molecule. The final structural parameters are listed in Tables 3 – 5. Lists of observed and calculated structure factors are available from BK or AMP on request.

Table 3. Positional and thermal parameters (x10^4) of the atoms in molecule A. The B_{ij} values refer to the temperature factor expression

$$\exp\{-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})\}.$$

Estimated standard deviations are given in parentheses.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
C(1)	10398(4)	-1615(4)	3012(2)	119(6)	81(4)	37(2)	36(4)	8(3)	12(2)
C(2)	11555(4)	-1307(4)	2314(3)	120(6)	99(5)	51(2)	43(4)	24(3)	14(3)
C(3)	10808(5)	-1493(4)	1426(3)	150(6)	88(4)	46(2)	51(4)	36(3)	20(2)
C(4)	8963(4)	-2040(4)	1272(2)	144(6)	72(4)	34(2)	34(4)	15(3)	10(2)
C(4A)	8573(4)	-944(4)	1932(2)	120(5)	67(4)	32(2)	36(4)	13(2)	8(2)
C(5)	8835(4)	447(4)	1537(2)	147(6)	73(4)	34(2)	47(4)	15(3)	11(2)
C(6)	10658(5)	1601(4)	1706(3)	166(7)	73(4)	36(2)	32(4)	22(3)	15(2)
C(7)	11569(5)	1973(4)	2695(3)	150(6)	83(5)	42(2)	13(4)	17(3)	13(2)
C(8)	10980(4)	1053(4)	3288(3)	135(6)	73(4)	38(2)	26(4)	16(3)	12(2)
C(8A)	9590(4)	-552(4)	2956(2)	122(5)	69(4)	31(2)	32(4)	16(3)	8(2)
C(9)	8183(4)	-3548(4)	1596(3)	130(6)	71(4)	38(2)	43(4)	10(3)	7(2)
C(10)	9066(4)	-3243(4)	2637(3)	134(6)	76(4)	36(2)	46(4)	19(3)	14(2)
C(11)	13380(6)	-823(6)	2624(4)	146(8)	179(8)	98(4)	72(6)	10(4)	-1(4)
O(12)	13862(8)	-1881(12)	2204(5)	166(12)	406(25)	93(6)	153(14)	19(6)	-42(8)
O(12')	13443(10)	-2080(9)	3115(5)	166(15)	165(15)	45(5)	115(15)	10(4)	0(6)
C(13)	12988(11)	-3340(9)	2443(6)	391(20)	258(15)	123(6)	216(15)	-27(8)	-15(7)
O(14)	13922(4)	-22(6)	3516(3)	107(6)	393(11)	60(3)	57(6)	-4(3)	-8(4)
O(15)	15693(7)	808(9)	3852(5)	151(9)	396(17)	100(5)	30(9)	-4(5)	-3(7)
C(16)	8199(3)	127(3)	556(2)	167(5)	96(4)	38(2)	53(3)	3(2)	17(2)
C(17)	6456(6)	-878(5)	279(3)	167(7)	135(6)	62(3)	59(6)	-18(4)	13(3)
O(18)	8039(4)	1093(3)	2066(2)	198(5)	86(3)	53(2)	80(4)	36(2)	23(2)
C(19)	8171(7)	2479(5)	1842(4)	340(12)	113(6)	95(4)	145(7)	63(5)	42(4)
O(20)	11344(4)	2227(3)	1101(2)	208(6)	134(4)	44(2)	17(4)	3(3)	35(2)
C(21)	11663(5)	1545(4)	4342(3)	163(6)	88(5)	40(2)	-1(4)	8(3)	4(2)
O(22)	13209(6)	2841(3)	4521(2)	184(5)	107(4)	46(2)	3(4)	-8(2)	6(2)
C(23)	14075(7)	3238(6)	5486(4)	252(11)	198(9)	51(3)	29(8)	-39(4)	-1(4)
C(24)	14019(4)	1784(3)	4819(2)	230(6)	123(4)	39(2)	40(4)	31(3)	7(2)
C(25)	10210(7)	2982(6)	4598(4)	198(8)	198(8)	54(3)	133(8)	18(4)	8(4)
O(26)	8492(3)	-4659(3)	1108(2)	195(5)	89(3)	37(2)	81(3)	15(2)	8(2)
C(27)	7898(7)	-5053(5)	102(3)	331(11)	134(6)	36(2)	119(7)	8(4)	-2(3)
O(28)	6469(3)	-4030(3)	1504(2)	118(4)	72(3)	74(2)	30(3)	10(2)	18(2)
C(29)	5482(6)	-5446(5)	1760(4)	145(7)	84(5)	89(3)	15(5)	9(3)	16(3)
O(30)	8738(4)	-4216(3)	3088(2)	285(7)	86(4)	40(2)	54(4)	20(3)	23(2)

Table 4. Positional and thermal parameters (x10^4) of the non-hydrogen atoms in B. The B_{ij} values refer to the temperature factor expression

$$\exp\{-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})\}.$$

Estimated standard deviations are given in parentheses.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
C(1)	6477(2)	-3750(4)	3440(3)	35(1)	173(6)	68(3)	19(2)	13(2)	13(3)
C(2)	7005(2)	-5051(5)	3960(3)	51(2)	194(7)	66(3)	32(3)	16(2)	28(4)
C(3)	7731(2)	-4025(5)	4617(3)	47(2)	240(8)	66(3)	42(3)	9(2)	35(4)
C(4)	7883(2)	-1743(4)	4802(3)	41(2)	217(8)	63(3)	23(3)	2(2)	26(4)
C(4A)	7865(2)	-959(4)	3488(3)	32(1)	178(7)	63(3)	22(3)	6(2)	15(3)
C(5)	8702(2)	447(4)	2891(3)	28(1)	192(7)	73(3)	18(2)	1(2)	25(4)
C(6)	8749(2)	-2935(4)	2294(3)	30(1)	235(7)	70(3)	31(3)	10(2)	16(4)
C(7)	8014(2)	-3986(4)	1370(3)	32(2)	202(7)	60(3)	26(3)	6(2)	7(3)
C(8)	7266(2)	-3601(4)	1508(3)	30(1)	202(7)	59(3)	17(3)	6(2)	23(3)
C(8A)	7073(2)	-2289(4)	2619(3)	30(1)	183(7)	60(3)	23(2)	8(2)	20(3)
C(9)	7134(2)	-1285(4)	5466(3)	48(2)	201(7)	60(3)	23(3)	13(2)	21(4)
C(10)	6321(2)	-2390(4)	4606(3)	42(2)	196(7)	68(3)	20(3)	17(2)	21(4)
O(11)	5621(2)	-4982(4)	2737(3)	36(2)	202(7)	80(3)	12(3)	17(2)	11(4)
O(12)	5719(2)	-6730(3)	1981(2)	42(1)	199(5)	105(2)	-4(2)	23(1)	-21(3)
C(13)	5168(3)	-8602(6)	2162(5)	68(3)	233(7)	96(4)	-1(4)	46(4)	-17(7)
O(14)	5329(1)	-3717(3)	1979(2)	31(1)	220(6)	107(2)	13(2)	24(1)	24(3)
C(15)	4457(3)	-4473(4)	1505(5)	37(2)	387(13)	173(6)	29(4)	-4(3)	21(7)
C(16)	9423(1)	0(3)	3757(2)	32(1)	215(5)	96(2)	18(2)	-8(1)	-3(3)
C(17)	9533(3)	2091(5)	4315(4)	48(2)	234(9)	127(4)	14(3)	-10(2)	-7(5)
O(18)	8686(1)	409(3)	1912(2)	33(1)	237(5)	86(2)	29(2)	16(1)	51(3)
C(19)	9384(3)	529(6)	1139(4)	42(2)	326(10)	135(4)	33(4)	37(2)	78(6)
O(20)	9347(2)	-3626(4)	2513(2)	38(1)	291(6)	116(3)	54(2)	-21(1)	-3(3)
C(21)	8164(2)	-5481(5)	310(3)	34(2)	234(8)	74(3)	23(3)	10(2)	16(4)
O(22)	7399(2)	-6727(3)	-351(2)	43(1)	269(6)	74(2)	14(2)	4(1)	-2(3)
C(23)	7054(3)	-8481(5)	244(4)	50(2)	243(9)	124(4)	19(3)	13(2)	-9(4)
O(24)	8624(2)	-4346(3)	-545(2)	58(1)	266(6)	90(2)	32(2)	36(2)	11(3)
C(25)	8945(2)	-5579(7)	-1472(4)	69(3)	360(12)	121(4)	38(4)	51(3)	-6(6)
C(26)	7006(2)	-2111(3)	6612(2)	65(2)	260(6)	58(2)	28(2)	15(1)	32(3)
O(27)	7732(3)	-1644(7)	7526(4)	84(3)	427(13)	74(4)	46(5)	-13(2)	46(6)
O(28)	7275(2)	855(3)	5638(2)	53(1)	194(5)	80(2)	24(2)	21(1)	6(3)
C(29)	6684(3)	1673(6)	6339(4)	66(2)	226(9)	99(4)	37(4)	32(2)	7(5)
O(30)	5625(2)	-2253(4)	4844(2)	42(1)	376(7)	117(3)	30(2)	23(2)	-45(4)

Table 5. Positional (x10³) and thermal (x10² Å²) parameters of the hydrogen atoms in *B*, with estimated standard deviations in parentheses.

ATOM	X	Y	Z	B
H(C2)	680(2)	-653(6)	375(3)	365
H(C3)	813(2)	-471(5)	505(3)	338
H(C4)	839(3)	-102(5)	525(4)	345
H(C4A)	781(2)	45(5)	367(3)	297
H(C8)	680(2)	-435(5)	88(3)	281
H(C8A)	674(2)	-135(5)	231(3)	258
H(C11)	521(2)	-547(5)	339(3)	338
H1(C13)	528(3)	-981(7)	161(5)	643
H2(C13)	457(3)	-858(7)	222(5)	643
H3(C13)	532(3)	-890(8)	299(5)	643
H1(C15)	436(3)	-585(7)	92(4)	542
H2(C15)	435(3)	-480(7)	218(4)	542
H3(C15)	429(3)	-351(7)	113(4)	542
H1(C17)	907(3)	224(7)	486(5)	643
H2(C17)	1004(3)	245(7)	474(5)	643
H3(C17)	948(3)	293(7)	366(5)	643
H1(C19)	944(3)	188(7)	82(4)	502
H2(C19)	929(3)	-68(7)	53(4)	502
H3(C19)	994(3)	69(6)	163(4)	502
H(C21)	849(3)	-638(5)	69(3)	353
H1(C23)	690(3)	-813(6)	111(4)	498
H2(C23)	657(3)	-934(6)	-29(4)	498
H3(C23)	744(3)	-938(6)	25(4)	498
H1(C25)	924(3)	-463(7)	-204(4)	578
H2(C25)	846(3)	-650(7)	-213(4)	578
H3(C25)	922(3)	-66(7)	-108(4)	578
H1(C27)	804(3)	-27(7)	766(4)	603
H2(C27)	754(3)	-218(7)	828(5)	603
H3(C27)	821(3)	-224(7)	723(4)	603
H1(C29)	693(3)	315(7)	650(4)	453
H2(C29)	613(3)	137(6)	587(4)	453
H3(C29)	664(3)	112(6)	714(4)	453

RESULTS AND DISCUSSION

The numbering system used throughout this article, and the bond distances involving the non-hydrogen atoms in the two compounds are given in Fig. 1, and the corresponding angles in Table 6 and 7, *A* and *B*, respectively. The two different molecular geometries found in *A*, resulting from the atomic positions of the disordered atom O(12) — *cf.* footnote in Table 2 — are given in Fig. 2; the molecular geometry

of *B* is given in Fig. 3. As seen from Figs. 2 and 3, the dimers have the *endo* configuration. This is consonant with the considerations given by Holmberg[6] for the dimerization of 2,4-cyclohexadienones, and with the results of X-ray structure determinations of Diels-Alder adducts of substituted *o*-quinols.[7-10] The *endo* configuration of the title compounds has simultaneously been established by Dr. H.-D. Becker (Chalmers University of Technology and University of Gothenburg, Gothenburg, Sweden) from photochemical studies.[2]

The disorder observed in the dimethoxymethyl group attached to C(2) in *A* is reflected in the high estimated standard deviations of the structural parameters and also in the distances measured in this group, *cf.* Fig. 1a. The different steric orientations of the dimethoxymethyl group containing the disordered atom may be described by the torsion angles $C(2) - C(11) - O(12) - C(13) = -60.8°$, $C(2) - C(11) - O(12') - C(13) = 73.4°$, $C(3) - C(2) - C(11) - O(12) = -63.7°$ and $C(3) - C(2) - C(11) - O(12') = -124.1°$. The corresponding torsion angles $C(2) - C(11) - O(14) - C(15)$ and $C(3) - C(2) - C(11) - O(14)$ are -166.5 and $148.4°$, respectively. The disordered group is neglected in the following discussion of the two structures.

As is also found in the related compounds discussed previously,[7-10] there are some elongated $C(sp^3) - C(sp^3)$ bonds around C(4a) and C(8a). In *A* the bonds C(1)-C(8a) and C(4)-
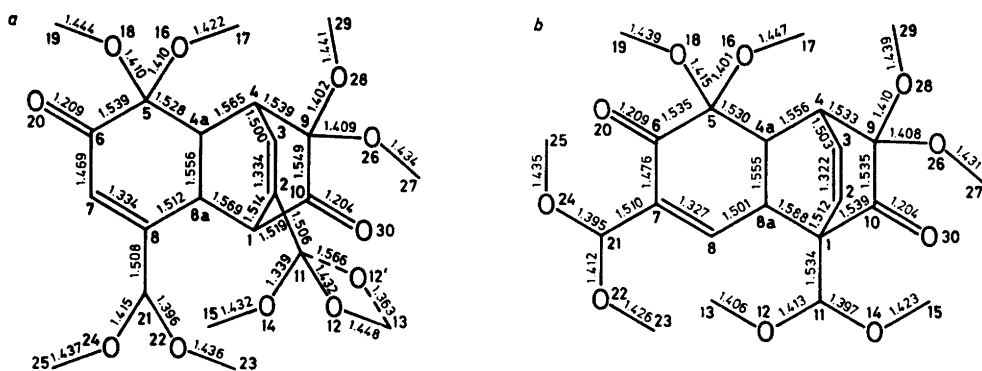

Fig. 1. Numbering system used and bond distances (Å) involving non-hydrogen atoms. *a*, Molecule *A*. The standard deviations are estimated to be less than 0.005 Å for all bonds except terminal C-O bonds for which they are 0.006 Å and the disordered dimethoxymethyl group where their values are less than 0.013 Å. *b*, Molecule *B*. The standard deviations are less than 0.004 Å, except for a few terminal C-O bonds where they are 0.005 Å.

Table 6. Bond angles (°) in molecule *A*. The standard deviations are estimated to be approximately 0.3° for the angles not involving the atoms C(11) − C(15), where they are c:a 0.6°.

C(2) − C(1) − C(8a)	107.4		C(4a) − C(8a) − C(8)	115.5
C(2) − C(1) − C(10)	104.4		C(4) − C(9) − C(10)	106.9
C(8a) − C(1) − C(10)	109.6		C(4) − C(9) − O(26)	113.9
C(1) − C(2) − C(3)	114.0		C(4) − C(9) − O(28)	107.4
C(1) − C(2) − C(11)	121.5		C(10) − C(9) − O(26)	104.5
C(3) − C(2) − C(11)	124.5		C(10) − C(9) − O(28)	112.4
C(2) − C(3) − C(4)	115.4		O(26) − C(9) − O(28)	111.7
C(3) − C(4) − C(4a)	110.5		C(1) − C(10) − C(9)	113.1
C(3) − C(4) − C(9)	106.8		C(1) − C(10) − O(30)	124.2
C(4a) − C(4) − C(9)	106.0		C(9) − C(10) − O(30)	122.8
C(4) − C(4a) − C(5)	112.2		C(2) − C(11) − O(12)	113.3
C(4) − C(4a) − C(8a)	109.7		C(2) − C(11) − O(12′)	105.5
C(5) − C(4a) − C(8a)	113.2		C(2) − C(11) − O(14)	109.5
C(4a) − C(5) − C(6)	111.5		O(12) − C(11) − O(14)	127.0
C(4a) − C(5) − O(16)	113.8		O(12′) − C(11) − O(14)	82.6
C(4a) − C(5) − O(18)	104.6		C(11) − O(12) − C(13)	112.4
C(6) − C(5) − O(16)	106.9		C(11) − O(12′) − C(13)	109.4
C(6) − C(5) − O(18)	108.3		C(11) − O(14) − C(15)	116.8
O(16) − C(5) − O(18)	111.6		C(5) − O(16) − C(17)	114.3
C(5) − C(6) − C(7)	113.4		C(5) − O(18) − C(19)	115.1
C(5) − C(6) − O(20)	123.1		C(8) − C(21) − O(22)	109.2
C(7) − C(6) − O(20)	123.3		C(8) − C(21) − O(24)	110.3
C(6) − C(7) − C(8)	121.7		O(22) − C(21) − O(24)	111.7
C(7) − C(8) − C(8a)	122.7		C(21) − O(22) − C(23)	112.6
C(7) − C(8) − C(21)	122.1		C(21) − O(24) − C(25)	115.1
C(8a) − C(8) − C(21)	115.2		C(9) − O(26) − C(27)	115.1
C(1) − C(8a) − C(4a)	108.5		C(9) − O(28) − C(29)	116.7
C(1) − C(8a) − C(8)	107.4			

Table 7. Bond angles (°) involving the non-hydrogen atoms in molecule *B*. The standard deviations are estimated to be approximately 0.3°.

|				
C(2) − C(1) − C(8a)	106.2		C(1) − C(8a) − C(4a)	108.9
C(2) − C(1) − C(10)	105.2		C(1) − C(8a) − C(8)	107.7
C(2) − C(1) − C(11)	113.9		C(4a) − C(8a) − C(8)	115.0
C(8a) − C(1) − C(10)	106.9		C(4) − C(9) − C(10)	107.1
C(8a) − C(1) − C(11)	114.5		C(4) − C(9) − O(26)	114.3
C(10) − C(1) − C(11)	109.4		C(4) − C(9) − O(28)	106.8
C(1) − C(2) − C(3)	115.2		C(10) − C(9) − O(26)	103.7
C(2) − C(3) − C(4)	115.1		C(10) − C(9) − O(28)	112.9
C(3) − C(4) − C(4a)	109.8		O(26) − C(9) − O(28)	112.1
C(3) − C(4) − C(9)	106.7		C(1) − C(10) − C(9)	113.6
C(4a) − C(4) − C(9)	107.5		C(1) − C(10) − O(30)	123.4
C(4) − C(4a) − C(5)	111.9		C(9) − C(10) − O(30)	123.0
C(4) − C(4a) − C(8a)	109.7		C(1) − C(11) − O(12)	110.3
C(5) − C(4a) − C(8a)	113.4		C(1) − C(11) − O(14)	107.7
C(4a) − C(5) − C(6)	110.8		O(12) − C(11) − O(14)	110.3
C(4a) − C(5) − O(16)	113.4		C(11) − O(12) − C(13)	115.9
C(4a) − C(5) − O(18)	105.5		C(11) − O(14) − C(15)	114.0
C(6) − C(5) − O(16)	107.5		C(5) − O(16) − C(17)	115.2
C(6) − C(5) − O(18)	108.4		C(5) − O(18) − C(19)	113.7
O(16) − C(5) − O(18)	111.2		C(7) − C(21) − O(22)	112.6
C(5) − C(6) − C(7)	113.0		C(7) − C(21) − O(24)	107.4
C(5) − C(6) − O(20)	123.4		O(22) − C(21) − O(24)	108.1
C(7) − C(6) − O(20)	123.5		C(21) − O(22) − C(23)	112.4
C(6) − C(7) − C(8)	119.6		C(21) − O(24) − C(25)	112.7
C(6) − C(7) − C(21)	116.9		C(9) − O(26) − C(27)	116.2
C(8) − C(7) − C(21)	123.6		C(9) − O(28) − C(29)	117.1
C(7) − C(8) − C(8a)	124.9			
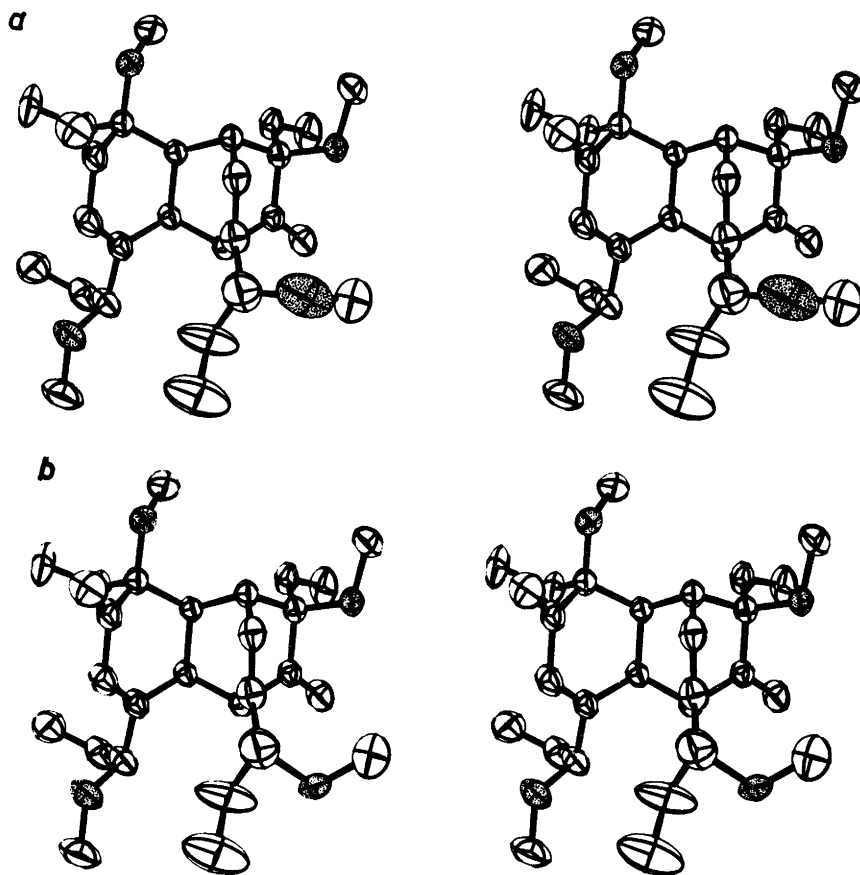
Fig. 2. Stereoscopic views of molecule *A*, calculated with the atomic positions O(12), *a*, and O(12′), *b*. The atoms O(12), O(12′), O(16), O(22) and O(26) are marked with shaded ellipsoids.
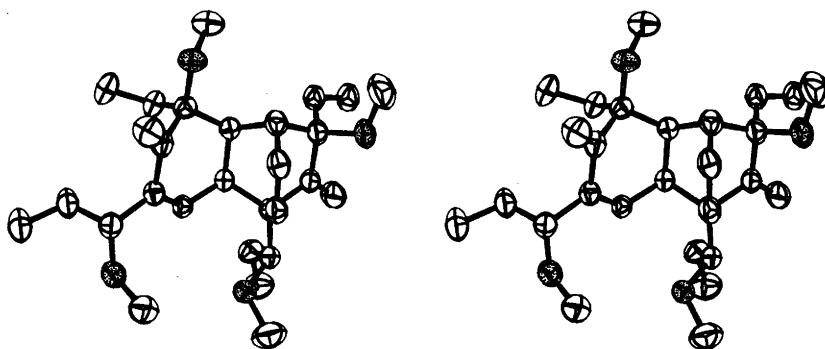

Fig. 3. Stereoscopic view of molecule *B*. The atoms O(12), O(16), O(22) and O(26) are marked with shaded ellipsoids.

C(4a) are 1.569 and 1.565 Å, respectively; they deviate more than 4σ from the mean ($=1.541$ Å) of the other $C(sp^3)-C(sp^3)$ bonds. In B the $C(1)-C(8a)$ bond length is 1.588 Å, which is significantly longer than the mean value, 1.542 Å, of the others. Some of the $C(sp^2)-C(sp^3)$ bond lengths are significantly longer than the standard value of 1.501 ± 0.004 Å given by Lide.[11] In A the bonds $C(5)-C(6)$ and $C(9)-C(10)$, 1.539 and 1.549 Å, respectively, deviate most from this standard value. In B the bonds $C(1)-C(10)$, $C(5)-C(6)$ and $C(9)-C(10)$ are 1.539, 1.535 and 1.535 Å, respectively. These elongations are probably due to the high degree of substitution (of non-hydrogens) at C(5) and C(9) in both molecules and in B also at C(1). Lengthening of the corresponding $C(sp^2)-C(sp^3)$ bonds is also observed in related compounds,[7-10] as well as the noted effect of conjugation in the $C(6)-C(7)$ bonds, which has lengths of 1.469 and 1.476 Å in A and B, respectively.

The four atoms C(4a), C(6), C(7) and C(8) are coplanar within ± 0.029 Å in A and within ± 0.011 Å in B. The atoms C(5) and C(8a) deviate from this plane by -0.64 and 0.15 Å, respectively, in A; and by -0.65 and 0.17 Å, likewise in B. This significant deviation from the plane for C(5) was also noted in related compounds.[7-10] The other three six-membered rings in the two molecules are boat-shaped. The dihedral angles between the least-squares planes based on the atoms C(4a), C(6), C(7), C(8) and C(2), C(3), C(4a), C(8a) are 79° in both molecules.

The hydrogen atoms in B lie in chemically reasonable positions; the mean value of the C-H bonds is 0.98 Å, range $0.88-1.05$ Å. No hydrogens were located in A.

The arrangements of molecules in the unit cells are shown in Fig. 4. Both structures are held together in the three dimensional space by van der Waals forces. There are, however, some intermolecular contacts (neglecting hydrogens) shorter than 3.3 Å in both compounds. In A these are $C(19^i)-O(26^{ii}) = 3.14$ Å and $C(25^i)-(30^{iii}) = 3.29$ Å; $i \equiv x,y,z$; $ii \equiv x,y+1,z$; $iii = 2-x, -y, 1-z$. In B they are $O(16^i)-O(16^{iii}) =$
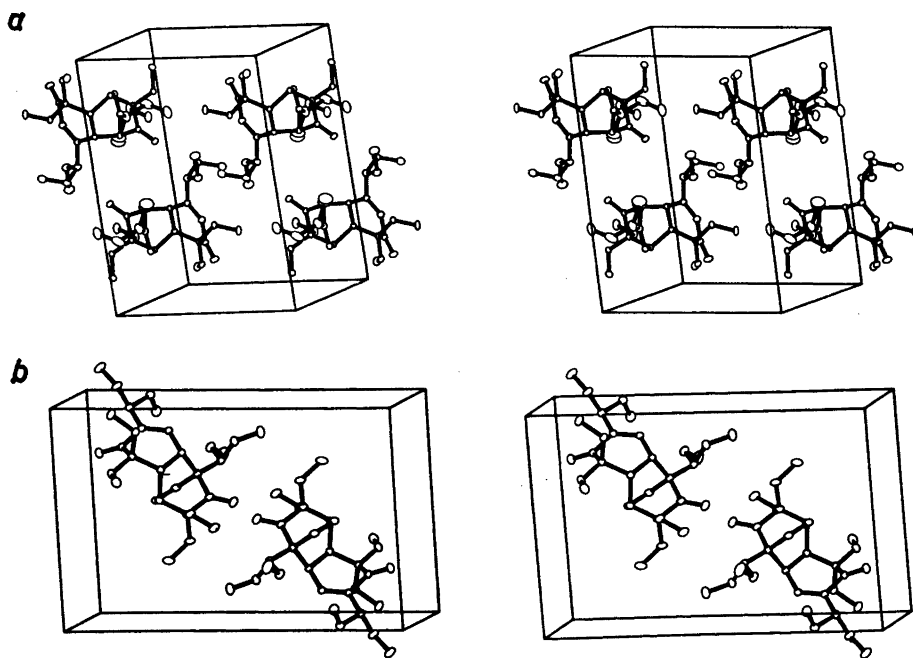

Fig. 4. Stereoscopic views of the molecular packing arrangements. (*a*) Compound A, calculated with the position of O(12), with *b* horizontal, *c* vertical and *a* towards the reader. (*b*) Compound B with *a* horizontal, *c* vertical and *b* downwards perpendicular to the plane of the paper.

3.15 Å, $O(16^i) - C(17^{iii}) = 3.26$ Å and $O(20^i) - C(25^{iv}) = 3.21$ Å, iv $\equiv 2\text{-}x,\text{-}y\text{-}1,\text{-}z$.

A further discussion of the crystal structures of 1,4-ethanonaphthalenes will be given in a forthcoming article.

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