Highly Alkylated Cyclohexanes. – X-Ray Crystal Structures, Force-Field Calculations, and Conformations of *cis*/*trans*-1,4-Disubstituted Cyclohexane Isomers

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The structures of mesylated *cis*- and *trans*-tetramethylshisool *cis*-**2** and *trans*-**2** have been elucidated by single-crystal X-ray techniques. In *cis*-**2** the isopropenyl group adopts an axial position in the crystal, and the structural data obtained are in good agreement with those from force-field calculations. In *trans*-**2** the two rotamers arising from rotation of the isopropenyl group were assigned by NOE measurements. Comparison of the spectroscopic data with those of other tetramethyllimonene derivatives showed that these can be classified into compounds with preferred equatorial and preferred axial position of the isopropenyl group.

Hochalkylierte Cyclohexane. – Röntgenstrukturanalyse, Kraftfeld-Berechnungen und Konformationen von *cis*/*trans*-1,4-disubstituierten Cyclohexan-Isomeren

Die Struktur von mesyliertem *cis*- und *trans*-Tetramethylshisool *cis*-**2** und *trans*-**2** wurde durch Einkristall-Röntgenmethoden aufgeklärt. In *cis*-**2** nimmt die Isopropenylgruppe im Kristall eine axiale Stellung ein, und die erhaltenen Strukturdaten stehen in gutem Einklang mit Kraftfeldberechnungen. In *trans*-**2** wurden zwei Rotamere, die durch Rotation der Isopropenylgruppe entstehen, durch NOE-Messungen zugeordnet. Der Vergleich der spektroskopischen Daten mit denen anderer Tetramethyllimonenderivate zeigt, daß diese in Verbindungen mit bevorzugt äquatorialer und bevorzugt axialer Lage der Isopropenylgruppe eingeordnet werden können.

The chemistry of tetramethyllimonenes (TM-limonenes) has posed interesting configurational and conformational problems, which made it desirable to obtain X-ray crystallographic information. For this purpose we have chosen two key compounds, i.e. the isomeric TM-shisools *trans*-**1** and *cis*-**1**. Although the two alcohols could be prepared stereoselectively, they did not form crystals suitable for X-ray crystallography. We therefore prepared the methanesulfonates *trans*-**2** and *cis*-**2** and have supported the experimental findings by force-field calculations on the alcohols *trans*-**1** and *cis*-**1**.

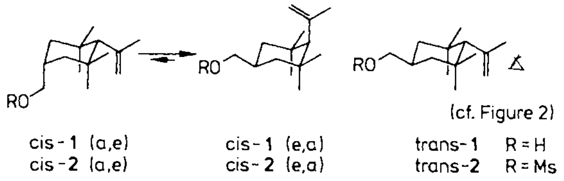


Figure 1 represents the structure of *cis*-**2** in the side view. Figure 2a shows the side view of *trans*-**2** whereas Figure 2b illustrates the shape of *trans*-**2** from another angle. The measured and calculated structural data are confronted in Table 1 and are interpreted as follows.

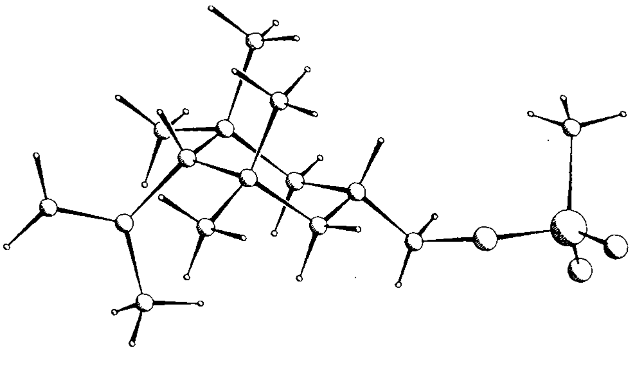


Figure 1. X-ray crystal structure of *cis*-**2**

Ring conformation: As suspected previously[1)], the isopropenyl group adopts an axial position in *cis*-**2**, whereas in *trans*-**2** it prefers the equatorial position. Apparently, *cis*-**2** (a,e) is destabilized relative to *cis*-**2** (e,a) because it contains an unfavourable interaction of the 1,3,5-*syn*-triaxial substituents and also an unfavourable interaction with the fixed isopropenyl group.

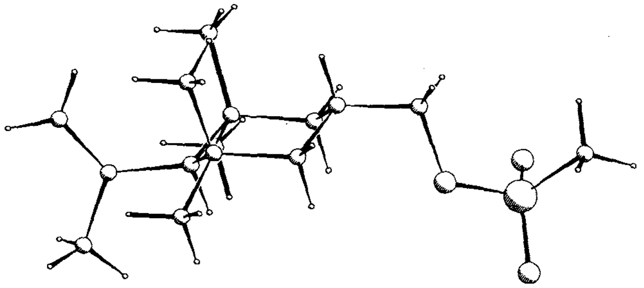


Figure 2a. X-ray crystal structure of *trans*-**2** (side view)

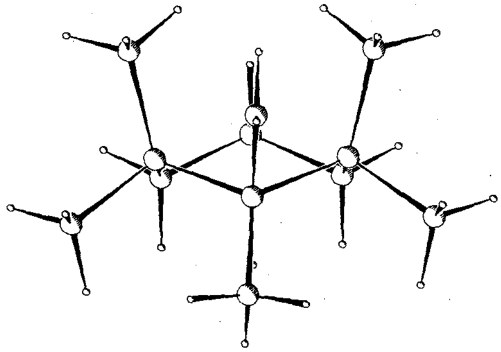
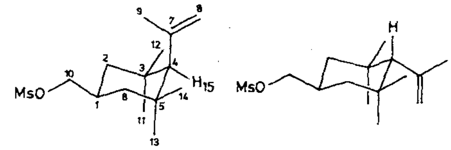


Figure 2b. View on the isopropenyl group in *trans*-**2** along the C(7)–C(4) bond axis [Atoms C(7) and C(4) coincide]

Ring flattening: As shown in Figure 2b, the *syn*-axial methyl groups repel each other strongly[2]. Their distance in *trans*-**2** is 3.35 Å compared with a distance of 2.64 Å of the quaternary ring carbons C(3) and C(5). Ring flattening shows up in the structural data, especially those of *cis*-**2** (e,a) (Table 1). The axial isopropenyl group causes a further deformation of the cyclohexane chair. The torsion angles within the ring are clearly smaller than the "ideal angle" of 60°. They are comparatively large near carbon C(1) (55.5–56.2) and small in the vicinity of carbon C(4) (44.1–44.5). In other words, puckering is most developed at C(1) and least near C(4). Parallel to puckering of the molecule, the internal bond angles are expanded, least at C(1) (110.7°), but more at the other ring carbons (111.3–114.4°). Furthermore, in *cis*-**2** the normal carbon-carbon bond length of 1.534 Å of cyclohexane has increased up to 1.566 Å in the vicinity of the quaternary carbons. The measured structural data of *cis*-**2** suggest that the compound is asymmetrically distorted in the crystal lattice. The measurements showed that two molecules were present in the unit cell, which differed in the position of CH_2OMs. In contrast, the unit cell of *trans*-**2** is smaller (820.6 vs. $1691.3 \cdot 10^6$ pm^3 for *cis*-**2**) and the molecule is symmetric within experimental error. The sum of the six internal torsion angles in *trans*-**2** (322.8) is closer to the "ideal value" of 360° than in *cis*-**2** (301.0°), i.e. *trans*-**2** is flattened less. It is noticeable that the C(3)–C(4)–C(5) bond angle has expanded to 116.0°.

Table 1. Selected experimental (X-ray crystallographic) vs. calculated (force-field) structural parameters of *cis*-**2** and *trans*-**2**



	cis-**2** exp.	*cis*-**2** calcd.	*trans*-**2** exp.	*trans*-**2** calcd.
	Torsions angles [°]			
9–7–4–15	177.9	0.0	176.4	177.2
1–2–3–4	50.8	48.6	53.2	50.1
2–3–4–5	44.5	42.4	50.8	43.4
3–4–5–6	44.1	42.4	50.9	44.4
4–5–6–1	50.8	48.6	53.1	52.2
5–6–1–2	56.2	55.7	57.3	60.9
6–1–2–3	55.5	55.7	57.5	59.8
Σ	301.0	293.4	322.8	310.8
	Bond angles [°]			
2–1–6	110.7	110.8	110.3	109.6
1–2–3	113.7	114.1	114.1	113.5
2–3–4	113.0	111.6	108.1	109.3
3–4–5	114.2	117.2	116.0	118.4
4–5–6	111.3	111.6	108.4	109.3
5–6–1	114.4	114.1	113.9	113.5
11–3–12	105.5	104.3	107.9	105.5
13–5–14	105.8	104.3	106.3	105.5
	Bond lengths [Å]			
1–2	1.525	1.536	1.510	1.535
2–3	1.516	1.544	1.537	1.548
3–4	1.562	1.560	1.561	1.558
4–5	1.566	1.560	1.557	1.560
5–6	1.540	1.544	1.534	1.548
6–1	1.510	1.536	1.517	1.536
	Nonbonding distances [Å]			
2–6	2.498	2.530	2.483	2.500
3–5	2.632	2.664	2.644	2.680
11–13	3.243	3.410	3.350	3.580

Rotamer population: In the crystal state *cis*-**2** as well as *trans*-**2** contain one rotamer each, i.e. α- and β-rotamer, respectively (cf. Table 2). In contrast, the force-field calculations suggest that the β-rotamer is a minimum for both compounds.

Force-field calculations: Table 1 shows satisfactory agreement of measured and calculated structural data. *cis*-**2** (e,a) with axial isopropenyl group is preferred according to the calculations and flattening of *cis*-**2** as well as *trans*-**2** is reproduced in qualitatively correct fashion. Only the extent of flattening is overestimated, and this could be due to an overestimation of nonbonded interactions of MM2[3].

*Spectroscopic determination of the conformation of cis-**2** in solution:* Crystal structure data and force-field calculations cannot necessarily be extrapolated to the solvated state. It is well-known that axial and equatorial protons clearly differ in their chemical shift. In *trans*-**2** the axial methylene protons at C(2) and C(6) resonate at 0.98 ppm and the equatorial ones at 1.53 ppm. Now in *cis*-**2** and *trans*-**2** the C(1) proton shows nearly the same chemical shift (2.11 and, respectively, 2.21 ppm), i.e. it is axial. Hence, *cis*-**2** exists preferentially as *cis*-**2** (e,a) in solution.

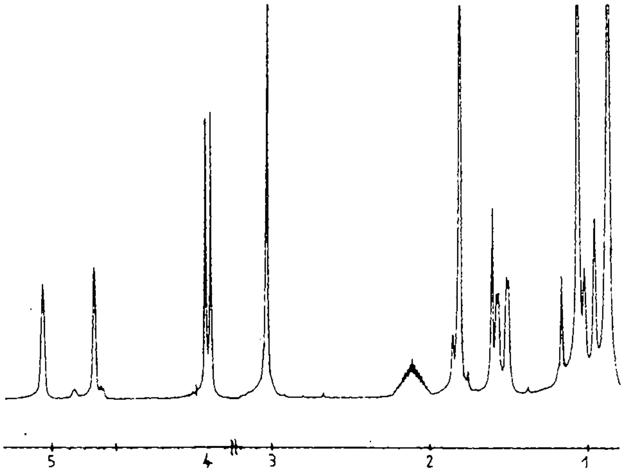
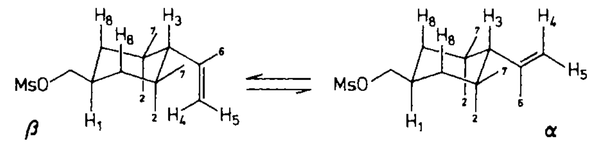


Figure 3. *trans*-**2**, 240 K

Table 2. NOE enhancements in *trans*-**2** at 240 K



Irradiation at δ	Proton	NOE δ	(%)	with Proton
0.87	H-7	1.81	(1)	H-6
1.06	H-2	2.12	(2)	H-1
		4.73	(1)	H-4
1.60	H-3	1.81	(5)	H-6
		0.94	(12)	H-8
1.81	H-6	1.60	(1)	H-3
		5.06	(1)	H-5
4.73	H-4	1.06	(8)	H-2
		5.06	(35)	H-5

*Hindered rotation of the isopropenyl group of trans-**2***: The X-ray crystal structure of *trans*-**2**, and the MM2 calculations suggest that the β-rotamer (cf. heading of Table 2) is populated preferentially, in contrast to a previous interpretation of solution spectra[4]. A NOE study of *trans*-**2** at low temperature proved informative. In *trans*-**2** the isopropenyl group is clearly equatorial and all proton signals are well-resolved at 200 MHz (Figure 3). At 240 K the rotameric equilibrium is frozen and the signals of the olefinic, allylic methyl, and axial methyl protons are split. The preferred rotamer, which according to integration is present to the extent of 89%, showed the enhancements of Table 2. Therefore,

a) the β-rotamer is energetically preferred in the crystal state and also in solution. This finding is at variance with a previous interpretation of the ^{13}C-NMR spectra[4].

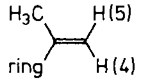
b) the assignment of the olefinic protons must be reversed: the proton *trans* to the methyl group (H-4) appears at 4.73 ppm, the *cis* proton H-5 at 5.06 ppm. Hence, the two rotamers of *trans*-**2** show the chemical shifts in Table 3.

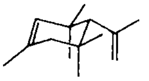
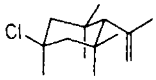
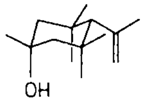
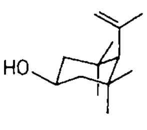
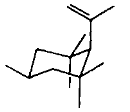
c) contrary to general experience, the axial methyl proton signals appear at lower field than the equatorial ones. This is probably a consequence of van der Waals repulsion and deshielding.

Table 3. Chemical shifts [δ, ppm] of olefinic protons in α- und β-rotamer of *trans*-**2**

H(4)β	H(4)α	H(5)β	H(5)α
4.73	4.68	5.06	4.86

Table 4. Chemical shift [δ, ppm] of olefinic protons in the α- and β-rotamer of tetramethyllimonene derivative at low temperature



		H(4)β	H(4)α	H(5)β	H(5)α
		Equatorial isopropenyl			
	trans-2	4.73	4.68	5.06	4.86
	3	4.78	4.67	5.04	4.86
	4	4.67	4.67	5.06	4.84
	5	4.79	-	5.07	-
	6	4.66	4.66	5.06	4.76
	7	4.80	4.66	5.07	4.88
		Axial isopropenyl			
	cis-1	4.74	4.64	4.84	4.60
	8	4.81	4.66	4.97	4.60
	9	4.76	4.62	4.84	4.58

Generalization of the spectroscopic measurements in the tetramethyllimonene series. Criteria for distinguishing axial and equatorial isopropenyl groups: As shown above, the isopropenyl group is equatorial in *trans*-**2** (e,e) [and in the derived alcohol *trans*-**1** (e,e)], whereas it is axial in *cis*-**2** (e,a) and in *cis*-**1** (e,a). As it turned out, *trans*-**2**, with its characteristic chemical shifts for the α- and β-rotamer (Table 3), is the prototype of a number of TML derivatives (Table 4) which show similar spectroscopic behaviour at low temperature, when the rotameric equilibrium is "frozen" on the NMR time scale: in **3**−**7** the isopropenyl group prefers the equatorial position. In **4**, **5**, and **6** the six-membered ring is saturated as in **8** and **9**. However, **8** and **9** behave spectroscopically like *cis*-**1**, i.e. the isopropenyl group is axial. Apparently, ring inversion in **8** and **9** does not pay energetically, because of the build-up of the *syn*-triaxial interaction. On the other hand, in **4**, **5**, and **6** a *syn*-triaxial interaction of substituents is present, irrespective of the position of the isopropenyl group.

Conclusions: Although the isopropenyl group is large, it cannot automatically be assumed to adopt the equatorial position. In the *cis*-1,4-disubstituted series *cis*-**1**, **8**, and **9** an equatorial isopropenyl group would cause an unfavourable *syn*-triaxial interaction of substituents. Instead, the isopropenyl group adopts the axial position.

We thank Dr. *E. Hofer* for the NOE measurements and the *Fonds der Chemischen Industrie* for financial support.

Experimental

trans-**2**: A solution of *trans*-TM-shisool (*trans*-**1**)[1] (0.32 g, 1.52 mmol) and DMAP (10 mg, 0.08 mmol) in absol. pyridine (3 ml) was cooled to 0 to −10°C, and methanesulfonyl chloride (0.22 g, 1.69 mmol) in 1 ml of pyridine was stirred in slowly. The mixture was stirred for 4 h at 0 to −10°C, then ice/water (5 ml) was dropped in, and the aqueous phase was extracted with ether (2 ×). The combined ether phase was washed with ice-cold 10% aqueous HCl (2x), aqueous $NaHCO_3$ and NaCl, and dried (Na_2SO_4). After removal of the solvent, the resulting yellow crystals were recrystallized from light petroleum to afford *trans*-**2**; colourless needles, 0.33 g (75%), mp 101−103°C. − 200-MHz ^{1}H-NMR ($CDCl_3$): δ = 0.88 (s, 6H, eq CH_3), 0.98 (d, 2H, ax CH_2), 1.08 (s, 6H, ax CH_3), 1.45−1.58 (m, 2H, eq CH_2), 1.6 (m, 1H, allyl CH), 2.0−2.33 (m, 1H, $CHCH_2O$), 3.02 (s, 3H, SO_2CH_3), 4.02 (d, J = 6 Hz, 2H, CH_2OMs), 4.73 (s, 1H, *trans*-$CH_2{=}CCH_3$), 5.03 (s, 1H, *cis*-$CH_2{=}CCH_3$).

cis-**2**: *cis*-TM-shisool (*cis*-**1**) (0.96 g, 4.57 mmol) and DMAP (34 mg, 0.27 mmol) in 10 ml of pyridine was allowed to react with methanesulfonyl chloride (0.65 g, 5 mmol) in 2.5 ml of pyridine, giving *cis*-**2** (1.1 g 84%), mp 53−54°C. − 200-MHz ^{1}H-NMR ($CDCl_3$) (because of hindered rotation, the signals are partially split and broadened considerably): δ = 0.91 + 0.96 (s, 6H, 2CH_3), 1.15 (s, 6H, 2CH_3), 1.26−1.51 (m, 4H, 2CH_2), 1.77 + 1.91 (m, 4H, allyl CH_3 + allyl CH), 2.07−2.24 (m, 1H, $CHCH_2OMs$), 3.02 (s, 3H, SO_2CH_3), 4.07 (d, J = 6 Hz, 2H, CH_2OMs), 4.55−4.95 (m, 2H, olefin H).

The intensities were measured in the ω-scan mode on a Siemens-Stoe-AED-2-Diffractometer with Mo-K_α radiation (graphite monochromator) and corrected as usual. The structure was determined by direct methods (MULTAN-80) and refined using the program system STRUCSY (STOE). The hydrogen atoms were refined iso-

Table 5. X-ray crystal data

	cis-**2**	*trans*-**2**
Recrystallized from	ether/light petroleum, 1:1	
Empirical formula	$C_{15}H_{28}SO_3$	$C_{15}H_{28}SO_3$
Molecular mass	288.5	288.5
Z	4	2
Space group	$P\bar{1}$	$P\bar{1}$
a [pm]	776.0(25)	638.4(28)
b [pm]	1283.8(55)	782.5(28)
c [pm]	1845.0(108)	1739.3(67)
α [°]	109.8(3)	95.0(3)
β [°]	100.2(4)	96.6(4)
γ [°]	92.5(3)	106.6(3)
V [$pm^3 \cdot 10^6$]	1691.3	820.6
Number of centered reflexions	38	26
Diffractometer	AED-2-Siemens-Stoe	
Temperature [°C]	21	21
Radiation used	Mo-K_α; λ = 71.069 pm; graphite monochromator	
Calculated density D_x [g/cm^3]	1.133	1.168
Scan mode	2.4°, ω	3.3°, ω
2Θ-range [°]	$2 \leqq 2\Theta \leqq 55$	$2 \leqq 2\Theta \leqq 55$
Number of reflexions measured	7963	4875
Number of observed reflexions ($F_o \geqq 3\sigma(F_o)$)	3810	3083
Number of variables	344	172
R	0.0940	0.0651
R_w, $w = 1/\sigma^2(F_o)$	0.0818	0.0549

Table 6. Local (× 10^4) and thermal parameters[a)] [pm^2] of *cis*-**2**

Atom	x/a	y/b	z/c	U_{eq}
S1	478(2)	5785(1)	1393(1)	601
01	-966(6)	5064(3)	854(2)	844
02	2052(6)	5338(3)	1593(3)	959
03	63(5)	6393(3)	2193(2)	693
C1	964(7)	6837(4)	1061(3)	737
H1a	1945(7)	7337(4)	1420(3)	811
H1b	1254(7)	6521(4)	552(3)	811
H1c	-45(7)	7237(4)	1022(3)	811
C2	-1906(7)	6597(5)	2194(3)	692
H2a	-2630(7)	5896(5)	2006(3)	762
H2b	-2288(7)	7017(5)	1864(3)	762
C3	-2062(6)	7219(4)	3033(3)	486
H3a	-1282(6)	7899(4)	3241(3)	534
C4	-3973(6)	7455(4)	3029(3)	550
H4a	-4688(6)	6749(4)	2821(3)	605
H4b	-4300(6)	7878(4)	2695(3)	605
C5	-4329(6)	8063(4)	3841(3)	538
C6	-3615(6)	7506(4)	4454(3)	563
H6a	-3471(6)	8098(4)	4953(3)	620
C7	-1712(7)	7156(5)	4426(3)	592
C8	-1490(7)	6582(4)	3572(3)	584
H8a	-2194(7)	5872(4)	3361(3)	642
H8b	-273(7)	6472(4)	3578(3)	642
C9	-3527(8)	9283(4)	4127(4)	806
H9a	-3745(8)	9671(4)	4642(4)	887
H9b	-2280(8)	9315(4)	4149(4)	887
H9c	-4060(8)	9627(4)	3768(4)	887
C10	-6335(7)	8104(5)	3770(4)	786
H10a	-6898(7)	7355(5)	3593(4)	864
H10b	-6593(7)	8521(5)	4271(4)	864

Table 6 (*Continued*)

H10c	-6765(7)	8448(5)	3395(4)	864
C11	- 286(7)	8165(5)	4836(3)	833
H11a	-436(7)	8530(5)	5366(3)	917
H11b	870(7)	7926(5)	4845(3)	917
H11c	-423(7)	8674(5)	4556(3)	917
C12	-1306(8)	6343(6)	4861(4)	1017
H12a	-1434(8)	6692(6)	5396(4)	1119
H12b	-2120(8)	5679(6)	4612(4)	1119
H12c	-124(9)	6153(6)	4855(4)	1119
C13	-4892(8)	6621(6)	4485(4)	739
C14	-5484(9)	5581(5)	3797(5)	1058
H14a	-4907(9)	5608(5)	3383(5)	1163
H14b	-5171(9)	4952(5)	3941(5)	1163
H14c	-6737(9)	5511(5)	3617(5)	1163
C15	-5546(9)	6771(7)	5137(4)	1077
H15a	-5157(9)	7451(7)	5576(4)	1185
H15b	-6370(9)	6220(7)	5173(4)	1185
S2	5772(3)	7394(2)	143(1)	823
C16	5430(10)	6094(6)	-549(6)	1537
H16a	5824(10)	6106(6)	-1011(6)	1691
H16b	6086(10)	5609(6)	-336(6)	1691
H16c	4199(10)	5826(6)	-684(6)	1691
O4	7483(7)	7898(4)	228(3)	1164
O5	5214(7)	7382(6)	797(3)	1543
O6	4701(-)	8054(-)	-289(-)	1813
C17	2911(-)	8070(-)	-419(-)	2381
H17a	2602(-)	8740(-)	-62(-)	2619
H17b	2344(-)	7435(-)	-356(-)	2619
C18	2388(12)	8025(7)	-1265(4)	1069
H18a	2867(12)	7402(7)	-1593(4)	1175
C19	449(12)	7690(6)	-1361(4)	1007
H19a	309(12)	7023(6)	-1242(4)	1108
H19b	-9(12)	8282(6)	-994(4)	1108
C20	-632(8)	7483(5)	-2177(4)	703
C21	-313(6)	8491(4)	-2437(3)	523
H21a	-636(6)	8189(4)	-3001(3)	575
C22	1664(7)	8965(5)	-2286(3)	593
C23	2641(7)	9051(6)	-1469(4)	832
H23a	3876(7)	9231(6)	-1430(4)	915
H23b	2214(7)	9644(6)	-1090(4)	915
C24	1768(8)	10129(5)	-2362(4)	984
H24a	1164(8)	10080(5)	-2876(4)	1082
H24b	1235(8)	10630(5)	-1970(4)	1082
H24c	2984(8)	10401(5)	-2283(4)	1082
C25	2614(8)	8228(5)	-2910(4)	846
H25a	1997(8)	8172(5)	-3423(4)	931
H25b	3809(8)	8543(5)	-2826(4)	931
H25c	2605(8)	7500(5)	-2873(4)	931
C26	-2605(9)	7269(5)	-2167(5)	1138
H26a	-3301(9)	7135(5)	-2681(5)	1252
H26b	-2806(9)	6637(5)	-2014(5)	1252
H26c	-2932(9)	7919(5)	-1796(5)	1252
C27	-132(9)	6395(5)	-2759(4)	983
H27a	-799(9)	6272(5)	-3277(4)	1081
H27b	1103(9)	6479(5)	-2759(4)	1081
H27c	-397(9)	5771(5)	-2608(4)	1081
C28	-1506(7)	9389(5)	-2162(4)	664
C29	-1415(8)	10022(5)	-1318(4)	919
H29a	-529(8)	9756(5)	-1012(4)	1010
H29b	-1110(8)	10800(5)	-1210(4)	1010
H29c	-2533(8)	9916(5)	-1183(4)	1010
C30	-2666(9)	9613(6)	-2705(5)	1079
H30a	-2710(9)	9193(6)	-3250(5)	1187
H30b	-3438(9)	10180(6)	-2561(5)	1187

[a] U_{eq} is calculated from the orthogonal U_{ij}-tensor $\exp[2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots 2hka^*b^*U_{12}\ldots)]$.

Table 7. Local (× 10^4) and thermal parameters[a] [pm^2] of *trans*-**2**

Atom	x/a	y/b	z/c	U_{eq}
S1	8836(1)	6985(1)	510	466
C1	7991(4)	7010(4)	-473(1)	583
H1a	6421(4)	6802(4)	-564(1)	641
H1b	8721(4)	8758(4)	-624(1)	641
H1c	8363(4)	6083(4)	-776(1)	641
O1	11138(3)	7293(3)	647(1)	942
O2	7422(3)	5434(3)	750(1)	684
O3	8490(2)	8715(2)	926(1)	493
C2	6246(4)	8846(4)	894(1)	521
H2a	5214(4)	7661(4)	801(1)	573
H2b	5957(4)	9518(4)	479(1)	573
C3	6005(4)	9777(3)	1662(1)	411
H3a	4588(4)	9983(3)	1587(1)	452
C4	6023(4)	8635(3)	2319(1)	488
H4a	4912(4)	7497(3)	2166(1)	537
H4b	7451(4)	8450(3)	2403(1)	537
C5	5615(4)	9486(3)	3096(2)	503
C6	7301(4)	11406(3)	3296(1)	392
H6a	8701(4)	11169(3)	3326(1)	431
C8	7723(4)	11599(3)	1889(1)	426
H8a	7669(4)	12311(3)	1468(1)	468
H8b	9145(4)	11401(3)	1970(1)	468
C9	3156(4)	9399(4)	3051(2)	781
H9a	2923(4)	9947(4)	3536(2)	860
H9b	2778(4)	10039(4)	2636(2)	860
H9c	2242(4)	8171(4)	2954(2)	860
C13	7311(4)	12326(3)	4105(1)	520
C7	7428(4)	12640(3)	2637(1)	390
C10	6126(7)	8354(4)	3730(2)	910
H10a	5874(7)	8848(4)	4224(2)	1001
H10b	5202(7)	7132(4)	3605(2)	1001
H10c	7648(7)	8388(4)	3759(2)	1001
C11	9479(5)	14274(3)	2864(2)	652
H11a	10743(5)	13858(3)	2978(2)	717
H11b	9676(5)	14983(3)	2439(2)	717
H11c	9318(5)	14995(3)	3316(2)	717
C12	5476(4)	13380(3)	2461(2)	559
H12a	5275(4)	14028(3)	2927(2)	615
H12b	5758(4)	14172(3)	2068(2)	615
H12c	4164(4)	12400(3)	2276(2)	615
C14	5712(5)	12981(4)	4316(2)	715
H14a	4438(5)	12881(4)	3944(2)	787
H14b	5841(5)	13558(4)	4837(2)	787
C15	9273(6)	12487(5)	4680(2)	926
H15a	10246(6)	11946(5)	4438(2)	1019
H15b	10029(6)	13732(5)	4856(2)	1019
H15c	8820(6)	11880(5)	5117(2)	1019

[a] U_{eq} is calculated from the orthogonal U_{ij}-tensor $\exp[2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots 2hka^*b^*U_{12}\ldots)]$.

tropically, all other atoms anisotropically. All parameters were finally refined with the weighting $w = 1/\sigma^2(F_o)$[5].

Force-field calculations were performed with the MM2 program[4].

CAS Registry Numbers

trans-**1**: 113831-04-2 / *cis*-**1**: 113831-05-3 / *trans*-**2**: 113831-06-4 / *cis*-**2**: 113831-07-5 / **3**: 68930-33-6 / **4**: 84602-70-0 / **5**: 83379-14-0 / **6**: 83379-15-1 / **7**: 96043-26-4 / **8**: 113831-08-6 / **9**: 113831-09-7

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[4] H. M. R. Hoffmann, R. J. Giguere, D. Pauluth, E. Hofer, *J. Org. Chem.* **48** (1983) 1155.

[5] Further details concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by specifying registry number CSD-52986, authors, and the reference to this publication.

[18/88]