

Chiral Induction in Photochemical Reactions. Part 4.¹ Conformational Analysis and Crystal Structure of (–)-8-Phenylmenthyl [(–)-(1*R*,2*S*,5*R*)-2-(1-Methyl-1-phenylethyl)-5-methylcyclohexyl] Phenylglyoxylates: their Face-differentiating Effect in Photochemical Oxetane Formation

Jan Runsink,* Hartmut Koch, Alfred Nehrings, and Hans-Dieter Scharf

Institute for Organic Chemistry, Technische Hochschule Aachen, Prof.-Pirlet-Strasse 1, 5100 Aachen, W. Germany

Ellen Nowack and Theo Hahn

Institute for Crystallography, Technische Hochschule Aachen, Jägerstrasse 17–19, 5100 Aachen, W. Germany

Depending on the solvent, the observed differences in the ¹³C n.m.r. chemical shifts of the 8,9-methyl† groups: $\Delta\delta_{8/9}$ in (–)-(1*R*,2*S*,5*R*)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexyl esters are used to gain information about the population P_A of conformation A in which the phenyl and ester groups point towards each other. The combination of ¹H n.m.r. high-field shifts with these P_A values provides valuable information about structural details. The generally accepted conformation A results from dipole–dipole-induced interactions. The ester residue is oriented so as to allow for maximum dipole–dipole-induced interaction. If there is no such interaction, one observes conformers B or C. The combined ¹³C and ¹H n.m.r. method described here is generally applicable for 8-phenylmenthyl esters. It is suited to explore the absolute configuration of the product oxetanes as well as the factors responsible for the face-differentiating effects of the chiral alcohol moiety. The crystal structure of (–)-(1*R*,2*S*,5*R*)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexyl phenylglyoxylate has been determined by single-crystal X-ray diffraction techniques using diffractometer data. The crystals are monoclinic with space group $P2_1$ and lattice parameters $a = 11.516(1)$, $b = 10.190(5)$, $c = 9.886(1)$ Å, $\beta = 114.12(1)^\circ$, final $R = 0.040$. The structure reveals that in this compound the phenylmenthyl moiety is frozen into conformation B. The bond lengths and angles are normal. The torsion angle for the two carbonyl groups is 103.3° .

In the photochemical addition of olefins to chiral α -ketoesters, diastereoselectivities $\geq 96\%$ can be obtained with chiral-inducing groups like (–)-8-phenylmenthyl [(–)-(1*R*,2*S*,5*R*)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexyl] instead of (–)-menthyl.¹ Similar results were observed in other chiral-controlled chemical reactions.^{2a–f} The role of the phenyl group in the (–)-8-phenylmenthyl moiety during the course of chiral induction is, however, not sufficiently understood. Thus, in the Lewis acid-catalysed Diels–Alder reaction of (–)-8-phenylmenthyl acrylates a so-called ‘ $\pi\pi$ ’-interaction between the phenyl group and the prochiral element was postulated.^{2b} It is still unclear whether the face-differentiating effect of the 1-methyl-1-phenylethyl rotator element in (1) is solely caused by a single conformation (e.g. A) through steric and/or other effects such as electronic, etc.

We therefore investigated the conformation of educts and products in the photochemical addition of olefins to chiral α -ketoesters in solution. For this purpose, a ¹³C–¹H n.m.r. method was developed, which can generally be applied to (–)-8-phenylmenthyl esters. Furthermore, by applying this method, it is possible to establish the absolute configuration of the product oxetanes. The crystal structure of (2a) was elucidated by means of X-ray analysis. We studied the following three aspects: (i), the face-differentiating conformation of the 1-methyl-1-phenylethyl group in (1) and (2); (ii), the position of the ester carbonyl group in (2) compared with the phenylmenthyl residue; (iii), the size of the interplanar angle between the ester carbonyl group and the substituent R in (2) in the solid state and in solution.

Conformer A is commonly assumed to be the face-differentiating structure in which the phenyl group is supposed to be opposite the substituent R. Therefore, high-field shifts of proton signals are observed upon suitable substitution. (–)-8-Menthyl esters of phenylglyoxylic acid also prefer conformation A except that the position of the phenyl group is substituted by a

proton. The observed ¹H n.m.r. high-field shifts of the signals are a function of factors (i)–(iii), in which case the ester conformation is generally assumed to be eclipsed.³

Results and Discussion

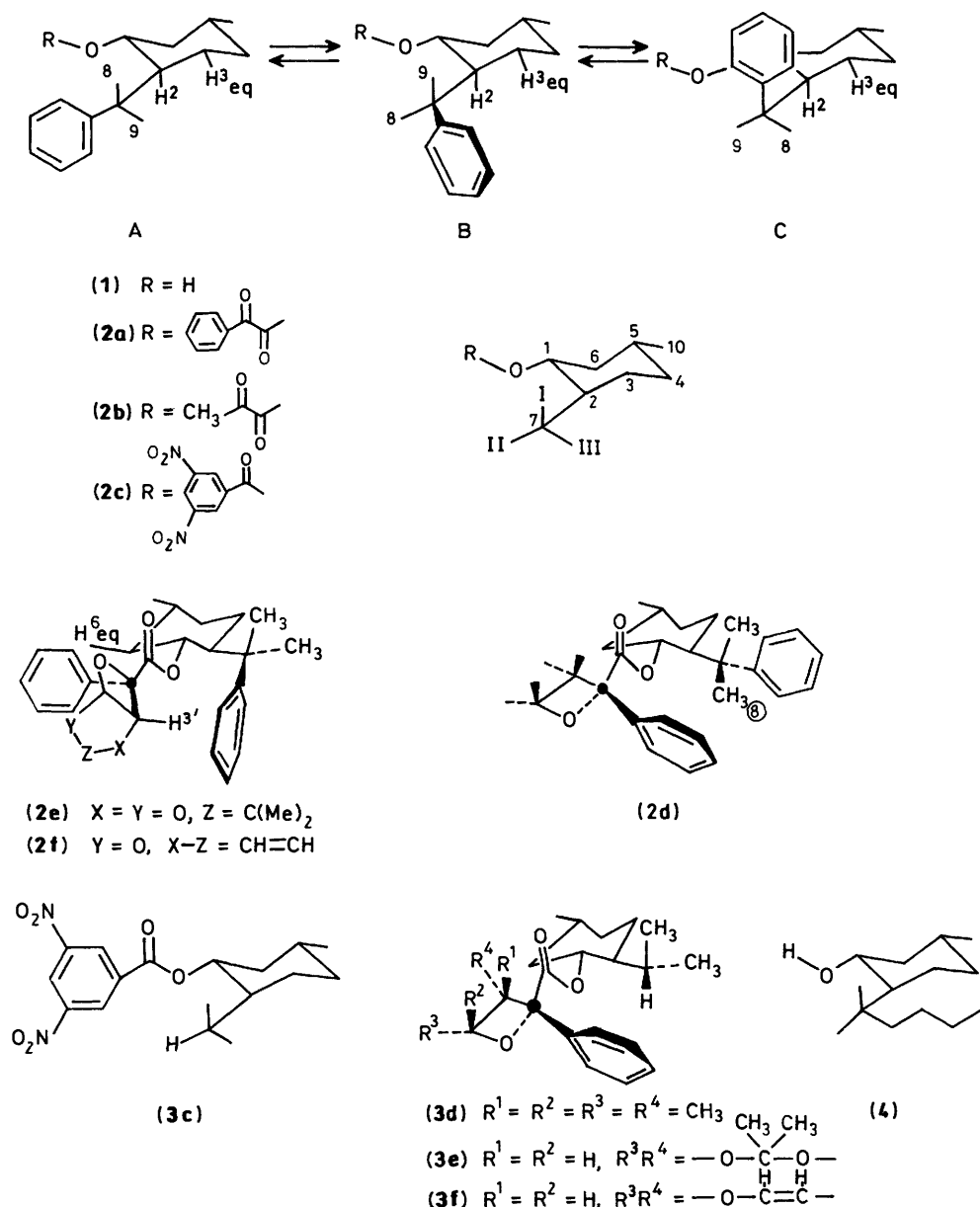
The ¹H and ¹³C n.m.r. chemical shifts of (–)-8-phenylmenthol (1), the ester derivatives (2a–f), the corresponding menthyl esters (3c–f), and (–)-8-n-butylmenthol⁴ (4) were measured (Table 1 and Experimental section). Correlated ¹³C 2D n.m.r. spectra were measured in order to obtain all ¹H chemical shift data. The spectra were run in CDCl₃ (all), DMSO [only (1)], benzene, and hexafluoropropan-2-ol (HFIP) [ester derivatives (2)] and in mixtures of these solvents.

The ¹³C n.m.r. signals of the C-8 and C-9 methyl† groups show a strong dependence on the substituent R and the solvent for compounds (1) and (2a–f) (Figure 1). The difference of the chemical shifts $\Delta\delta_{8-9}$ varies from -11.25 to $+7.57$ p.p.m.

The ¹H chemical shifts of the cyclohexane ring protons 2- and 3- H_{eq} indicates again the strong dependence on R and on the solvent, and a clear correlation with $\Delta\delta_{8-9}$ is recognized (Figure 2).

The CH₃ groups as well as the phenyl group can occupy positions I–III in conformations A–C. Thus, a CH₃ group in position I with two γ -syn-neighbours has a smaller δ value compared with a CH₃ group in positions II and III with one γ -syn-neighbour each. It is reasonable to state that for position II the δ -syn-neighbour results in a smaller δ value than for position III. The large value of $\Delta\delta_{8-9}$ in the ¹³C n.m.r. spectrum [up to -11.25 p.p.m. for (2c)] requires a large γ -syn-increment.⁵ The strong steric hindrance of the C-8 and C-9 methyl groups is

† Crystallographic numbering (see structural formulae, and Figures 4 and 5).



responsible for this. Steric hindrance also causes slow rotation of these CH₃ groups as indicated by the small relaxation times T_1 and by line broadening of the CH₃ resonances. T_1 Values for C-8 and C-9 methyls are almost equal to those for the (-)-8-phenylmenthyl CH₂ groups.⁶

In the ¹H n.m.r. spectrum the phenyl group of the (-)-8-phenylmenthyl moiety will shield 3-H_{eq} in conformation B and deshield 2-H in conformations A and B. For (2c) only conformation A exists at low temperature, since the $\Delta\delta_{8-9}$ value asymptotically approaches -11.25 p.p.m. on lowering the temperature, and since the chemical shifts of 2-H and 3-H_{eq} are the largest observed (Table 1). On the other hand, $\Delta\delta_{8-9}$ is +7.57 p.p.m. for (1) in DMSO and +7.43 p.p.m. for (2d) in CDCl₃ or benzene as solvent. The ¹H chemical shifts of 2-H and 3-H_{eq} are likewise small. Since the average of δ_8 and δ_9 is larger for (1) (DMSO) and (2d) than for (2c), it follows that an equilibrium exists between conformations B and C, whereas the contribution of conformation A is negligible. So the value of $\Delta\delta_{8-9}$ is a measure of the population P_A of conformation A ($0 \leq P_A \leq 1$; $P_A + P_B + P_C = 1$). Straightforward analysis shows that the value of P_A is $(\Delta\delta_{\max.} - \Delta\delta_{8-9})/(\Delta\delta_{\max.} - \Delta\delta_{\min.}) = (7.57 -$

$\Delta\delta_{8-9})/18.83$ if we assume that the ratio $P_B:P_C$ is invariant at constant temperature and that the $\Delta\delta_{8-9}$ values in the pure conformations A—C are constant with variation of the substituent R. $\Delta\delta_{\min.}$ is -11.25 p.p.m. for (2c), representing the largest negative value and $\Delta\delta_{\max.}$ is +7.57 p.p.m. [(1) in DMSO], representing the largest positive value. The P_A values obtained in this way are shown in Figure 1. The calculated P_A value is invariant towards a change in standard, and therefore towards a change in solvent. The determination of the ratio $P_B:P_C$ is not easy indeed, but P_B must clearly be larger than P_C .

The conformation of the ester carbonyl group of (2c) should be eclipsed with the C-1-H bond (Figure 3) because the mutual ring current shields the aromatic protons in the ¹H n.m.r. spectrum. The origin of the stabilization of conformation A is clearly a dipole-dipole-induced interaction.* The P_A values of esters (2) increase on adding HFIP and decrease on adding benzene. With HFIP, a strong hydrogen-bond-donating

* Dipole-dipole-induced interactions are an example of 'π-stacking'.^{2b} Orientation by several types of dipoles is possible. See for instance oxetane (2e)

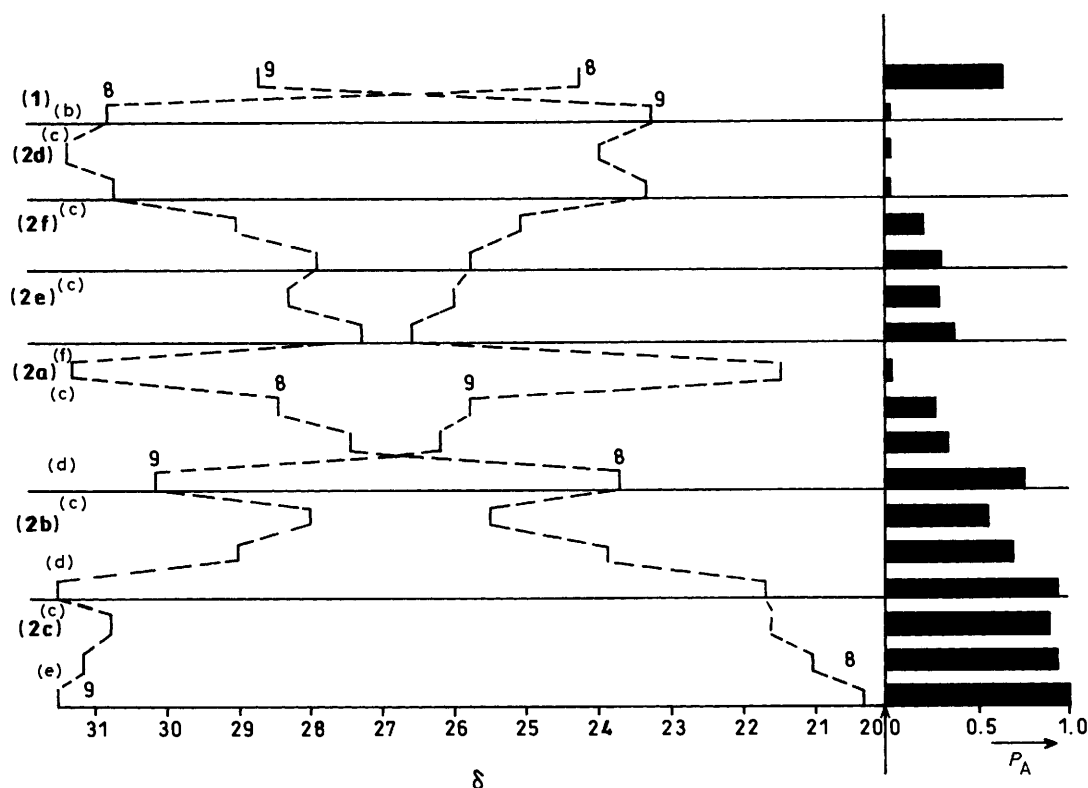


Figure 1. ^{13}C N.m.r. chemical shifts of C-8 and C-9 methyl groups of (1) and (2a–f) together with the calculated P_A values: (a) crossing of δ_8 and δ_9 was proven by measuring spectra in appropriate solvent mixtures, solvent CDCl_3 , unless otherwise mentioned; (b) $[\text{}^2\text{H}_6]\text{DMSO}$; (c) $[\text{}^2\text{H}_6]\text{-benzene}$; (d) HFIP; (e) -20°C (otherwise room temperature); (f) solid state (P_B 1)

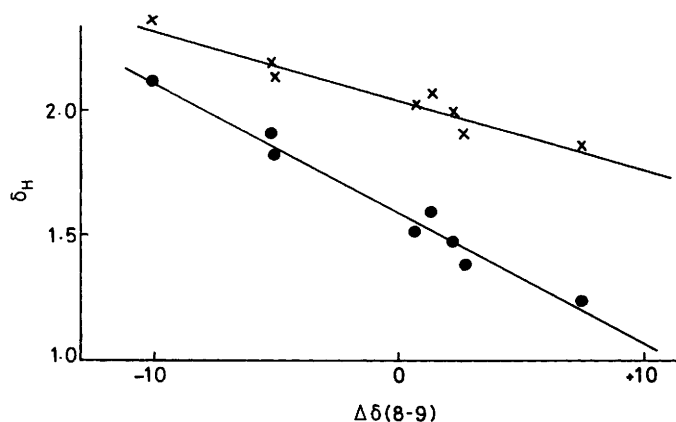


Figure 2. Correlation of the ^1H n.m.r. chemical shifts of 3- H_{eq} (●) and 2- H (×) with the ^{13}C difference in the chemical shifts $\Delta\delta_{8-9}$ of (1) and (2a–f): solvent CDCl_3 , (2a) also measured in C_6D_6 and a mixture of CDCl_3 –HFIP as solvent

solvent,⁷ the dipole–dipole-induced interaction is strengthened. On the other hand, benzene as solvent provides a stabilizing effect for the ester group thus destabilizing conformation A. The only case where no change in P_A is observed with benzene as solvent is (2d) since the value $P_A = 0$ has been reached for CDCl_3 . Likewise $P_A = 0$ is observed for (1) in DMSO. Conformation A of (1) is stabilized in CDCl_3 by an intramolecular hydrogen bond with the phenyl ring (P_A 0.64).

Solid-state Investigation.—In the solid state (2a) is frozen into conformation B as demonstrated by an X-ray crystal structure determination and a solid-state CP-MAS ^{13}C n.m.r. spectrum.

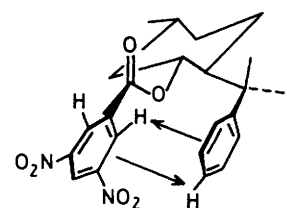


Figure 3. Conformation of (2c); the arrows represent the mutual shielding of the aromatic rings in the ^1H n.m.r. spectrum

However, from the CP-MAS ^{13}C n.m.r. spectrum alone, the possibility that (2a) was frozen into conformation A could not be ruled out.

The structure of (2a) as determined by single-crystal X-ray diffraction techniques is given in Figures 4 and 5. Bond lengths are reported in Figure 5a (standard deviations range between 0.001 and 0.005 Å) and bond angles in Figure 5b (standard deviations range between 0.1 and 0.2°). Important conformational features are as follows. (1) The phenylmethyl moiety of (2a) is frozen into conformation B. The torsion angle C(11)–C(7)–C(2)–C(3) is only $-47.6(2)^\circ$ resulting in short intramolecular distances for C(3)–C(12) [3.490(3) Å] and C(3)–C(16) [3.499(3) Å] (for atom numbering see Figure 5a). (2) The torsion angles between C(16)–C(11) and C(7)–C(2), C(7)–C(8), C(7)–C(9) are $-67.8(2)$, $52.3(2)$, and $169.6(2)^\circ$, respectively. (3) The phenyl ring of the phenylglyoxylate moiety is coplanar with the keto carbonyl group [within 0.125(3) Å]. (4) The torsion angle between the two carbonyl groups O(21)–C(20)–C(18)–O(19) is $-103.3(2)^\circ$. (5) The ester carbonyl group is *syn*-coplanar with the ester C–O bond [torsion

angle O(19)–C(18)–O(17)–C(1) $-1.4(2)^\circ$]. (6) The deviation from the eclipsed conformation of the ester C–1–H bond and the ester carbonyl group is $23.2(2)^\circ$ in the direction of C(6). (7) The keto carbonyl group points towards the C-8 methyl group of the phenylmenthyl moiety. (8) The thermal motion of most atoms is nearly isotropic, with the following notable exceptions for anisotropic vibrations: atom C(10) has its maximal root mean square amplitude of $0.482(5)$ Å nearly perpendicular to the average plane of the cyclohexyl ring, the other two amplitudes being $0.258(2)$ and $0.302(2)$ Å. For O(19) and O(21) the largest amplitudes of $0.419(2)$ Å and $0.420(3)$ Å occur perpendicular to the O(19)–C(18)–C(20) and C(18)–C(20)–O(21) planes, respectively (the other amplitudes ranging from 0.23 – 0.28 Å). (9) Various chemical groups are virtually planar: the phenyl ring C(22)–C(27) is planar within $0.003(3)$ Å, with C(20) deviating by $0.027(3)$ and O(21) by $0.125(3)$ Å. The phenyl ring C(11)–C(16) including C(7) is planar within 0.06 Å.

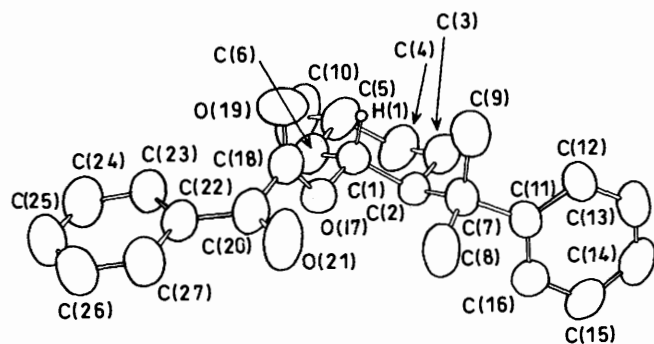


Figure 4. Molecular structure of (2a) with contours of temperature ellipsoids. View showing the chair form of the cyclohexane ring, and the C(1)–H(1), C(18)–O(19), and C(7)–C(9) bonds being approximately parallel. Hydrogen atoms except 1-H omitted

A comparison of this structure with that of (–)-8-menthyl *p*-bromophenylglyoxylate⁴ reveals that points (3)–(5) are the same for both molecules, and that the ester carbonyl group is practically eclipsed in the menthyl ester as well [point (6)]. A striking difference in structure, however, is the reversed sign of the dihedral angle between the carbonyl groups [points (4) and (7)]. The bond lengths and angles for both molecules are comparable; the variations in the individual bond lengths, however, are much smaller for (2a). No disorder (splitting of an atom) was observed for (2a) in contrast to other molecules.⁸

Intermolecular contacts have the dimensions of van der Waals separations or larger. The molecules of (2a) are packed in the crystal in such a way that the two types of phenyl rings are close to each other, thus allowing intermolecular dipole–dipole-induced interactions. Short intermolecular distances are presented in Figure 6. All other C–C and C–O intermolecular separations are larger than 3.60 Å [with the exception of one C(10)–O(21) distance of $3.537(4)$ Å]. No intermolecular H–H contacts are smaller than 2.57 Å; the intermolecular H–H distances between phenyl groups are larger than 2.64 Å, *i.e.* the hydrogens are not interfering with the π – π interactions.

Investigations of Product Oxetanes.—The determination of the ester carbonyl conformation (ii), the conformation of the substituent R (iii), and the absolute configuration of the product oxetanes (2e and f) can now be accomplished using the calculated P_A values as follows. The 3'-H signal of (2e and f) is shielded with respect to the corresponding signals of the menthyl ester (3e and f) ($\Delta\delta_3$). When HFIP is added dropwise to the solution, both the shielding of 3'-H and the P_A value are enlarged. $\Delta\delta_3$ is linearly related to P_A and $\Delta\delta_3 = 0$ when $P_A = 0$ as expected (Figure 7). The ratio $\Delta\delta_3 : P_A$ represents the shielding effect of 3'-H for the phenylmenthyl moiety populating conformation A.

The high ratio of -2.02 p.p.m. for (2e) and -1.74 p.p.m. for (2f) prove that 3'-H must be in the centre of the shielding cone

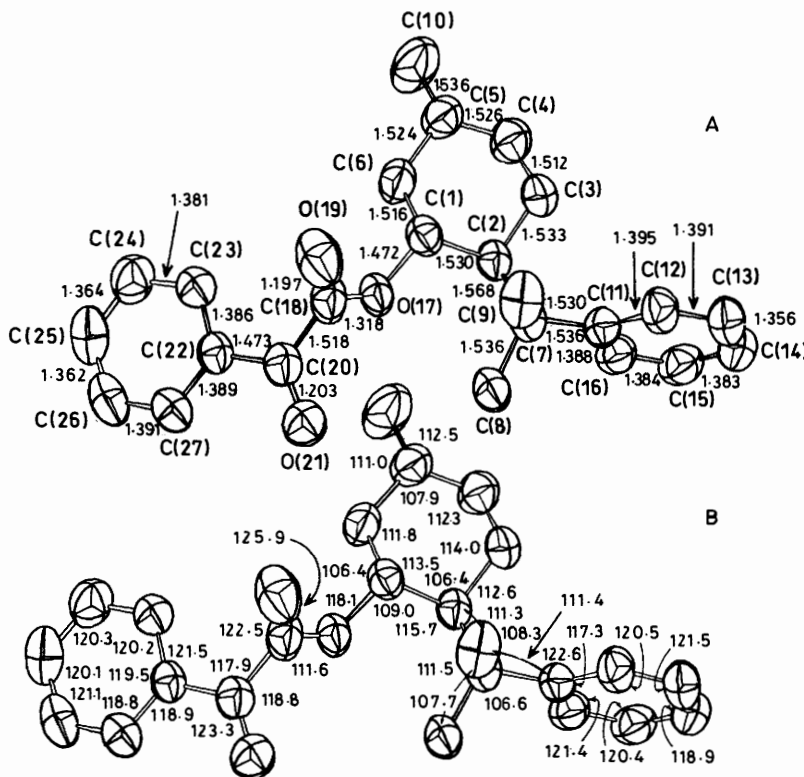


Figure 5. Molecular structure of (2a) with temperature ellipsoids reporting (a) bond lengths and (b) bond angles. Hydrogen atoms are omitted

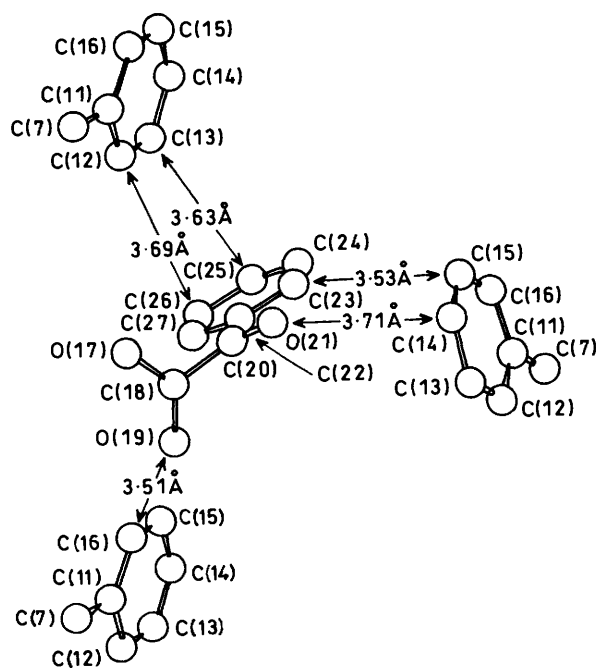


Figure 6. Intermolecular contacts of the phenyl groups. Small C-C and C-O separations are given indicating dipole-dipole-induced interactions. Projection along a

close to the phenylmethyl phenyl ring.⁸ As can be seen from molecular models, this is only possible if the conformation and configuration are as shown in Figure 6. The ester carbonyl group must be nearly eclipsed with respect to the C-1-H bond. The *R* configuration of (2c) was also proven by chemical degradation.^{1b}

If the phenylmethyl moiety does not populate conformation A, then the conformation of the ester substituent R (iii) of the product oxetanes (2d-f) is different from that depicted. (1) One observes shielding of 6-H_{eq} with increasing P_A for (2e and f) (Figure 8). (2) However, for (2d) (P_A 0) and (3d-f) the shift of 6-H_{eq} is nearly constant (δ 1.94–2.05). (3) The shift of 6-H_{eq} for (1) in DMSO (δ 1.80 for P_A 0) and in CDCl₃ (δ 1.83 for P_A 0.64) and for (4) in CDCl₃ (δ 1.90 p.p.m.) are also nearly equal.

The shielding of 6-H_{eq} in (2e and f) must be caused by the 2-Ph ring. If the phenylmethyl moiety populates conformation A, the ester group R is rotated in such a way that the 2-Ph approaches 6-H_{eq}.

If the phenylmethyl moiety does not populate conformation A, then 2-Ph is close to C-8 and C-9 methyls and since conformation B now dominates one observes strong shielding in the ¹H spectrum of 8-H₃ and to a smaller extent of 9-H₃ (Figure 8). The sign of the interplanar angle of 2-Ph with the carbonyl group differs for the conformations depicted. The absolute value of these angles however are about the same. The conformation of the ester group of (2d) changes to that depicted when benzene is used as solvent, in order to solvate the oxetane dipole. One now observes normal chemical shifts for 8- and 9-H₃ (δ_8 1.13, δ_9 1.09). The Cahn-Ingold-Prelog absolute configuration is *S* for oxetane (2f) and *R* for (2d and e). All these oxetanes, however, are formed by *re*-attack⁹ of the keto carbonyl group of (2a).

Conclusions.—The population P_A of conformation A of the (–)-8-phenylmethyl moiety in phenylglyoxylates can be easily derived from the ¹³C chemical shifts of 8- and 9-H₃. Conformation A is only populated if it is stabilized by a dipole-dipole-induced interaction and if it is not destabilized by steric

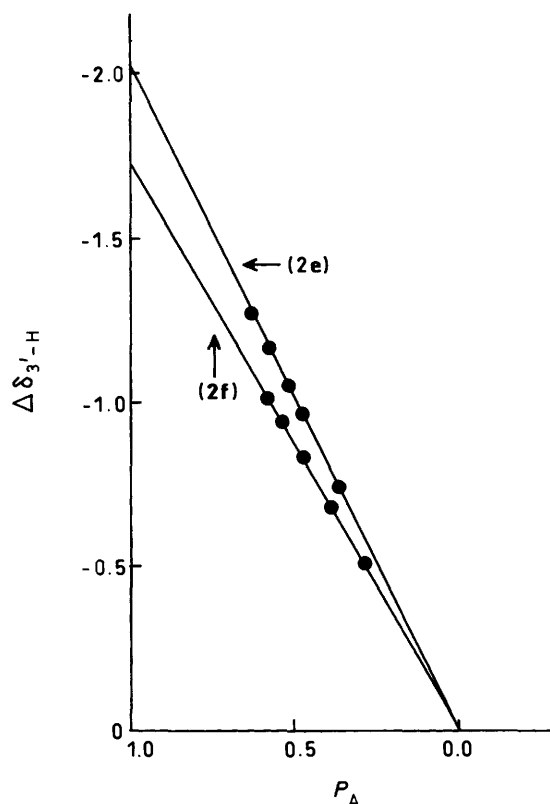


Figure 7. Correlation of P_A with the shielding of the 3'-H signal in the ¹H n.m.r. spectrum of (2e and f) with respect to (3d and f) when HFIP is added dropwise to the CDCl₃ solution

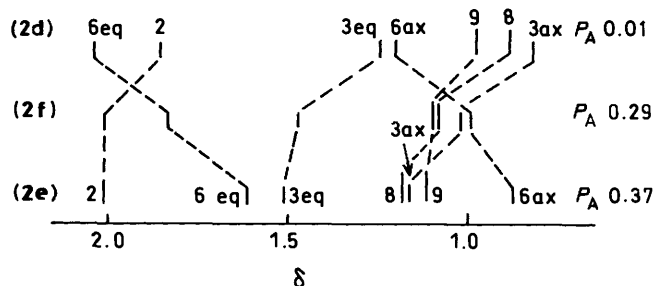


Figure 8. Typical ¹H n.m.r. chemical shifts of (2d–f) (CDCl₃)

repulsion. The dipole-dipole-induced interaction is also able to orientate the conformation of the ester moiety of compounds (2).

The pure steric face-differentiating shielding effect of (–)-8-phenylmethyl is caused by the C-8 and C-9 methyl groups only and should therefore be equal to that with (–)-8-*n*-butylmethyl. Increased diastereoselectivity in oxetane formation, with (–)-8-phenylmethyl compared with (–)-8-*n*-butylmethyl as the chiral alcohol moiety, must be attributed to the electronic effect of the phenyl ring. For (2b) (P_A 0.54) a clear increase in diastereoselectivity was observed; for (2a) (P_A 0.26) the increase was, however, small¹⁰ (solvent benzene). The P_A values change during the course of the oxetane formation (Figure 1). The P_A values in the transition state will depend on the amount of charge polarization and steric repulsion present. Consequently face-differentiating shielding turns out to be a dynamic process.

Experimental

Varian EM-390, CFT-20, and XL-400 and Bruker Am-500, Am-300, Am-200, and WM-400 instruments were used for n.m.r.

Table 1. ¹H Chemical shifts^a

Compd.	1-H	2-H	3-H _{ax}	3-H _{eq}	4-H _{ax}	4-H _{eq}	5-H	6-H _{ax}	6-H _{eq}	8-H	9-H	10-H	P _A
(1)	3.50	1.68	1.02	1.67	0.82	1.62	1.38	0.93	1.83	1.42	1.29	0.87	0.64
<i>b</i>	3.34	1.48	0.72	1.08	0.64	1.41	1.28	0.95	1.80	1.45	1.32	0.80	0.00
(4)	3.53	1.14	0.97	1.72	0.81	1.63	1.42	0.97	1.90	0.92	1.01	0.88	
(2a)	5.03	2.07	1.09	1.60	0.86	1.60	1.51	1.20	2.13	1.37	1.31	0.91	0.33
<i>c</i>	5.04	1.91	0.83	1.39	0.58	1.30	1.13	1.04	2.12	1.38	1.26	0.71	0.26
<i>d</i>	5.05	2.20	1.23	1.91	0.97	1.74	1.55	1.23	2.05	1.30	1.21	0.93	0.68
(2b)	4.85	2.14	1.16	1.83	0.92	1.67	1.46	1.10	1.83	1.31	1.21	0.88	0.68
(2c)	5.25	2.37	1.35	2.13	1.08	1.84	1.60	1.22	1.92	1.33	1.18	0.96	0.94
(2d)	4.78	1.86	0.82	1.25	0.71	1.43	1.40	1.21	2.05	0.88	0.98	0.85	0.01
(2e)	4.81	2.03	1.17	1.52	0.78	1.52	1.28	0.88	1.62	1.19	1.12	0.77	0.37
(2f)	4.86	2.02	1.02	1.48	0.79	1.55	1.41	1.00	1.84	1.09	1.09	0.82	0.29
(3d)	4.73	1.38	0.95	1.60	0.84	1.64	1.45	1.13	1.94	0.38	0.65	0.89	
(3d') ^e	4.79	1.46	1.00	1.66	0.83	1.66	1.43	0.95	1.83	0.64	0.79	0.84	
(3e)	4.70	1.39	1.02	1.64	0.86	1.68	1.45	0.99	1.93	0.58	0.77	0.88	
(3f)	4.82	1.40	0.97	1.65	0.86	1.65	1.48	1.07	2.00	0.55	0.72	0.89	

^a Solvent CDCl₃ unless otherwise mentioned. ^b [2H₆]DMSO. ^c [2H₆]Benzene. ^d CDCl₃-HFIP. ^e Minor isomer.

Table 2. ¹³C N.m.r. chemical shifts^a

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Ph-1	Ph-2	Ph-3	Ph-4
(1)	72.97	54.23	26.51	34.92	31.53	45.43	39.80	24.28	28.73	22.00	151.34	125.81	128.46	125.81
<i>b</i>	71.42	52.88	26.82	34.49	31.17	46.35	40.51	30.85	23.28	21.97	150.92	125.74	127.66	124.83
(2a)	77.40	50.52	26.88	34.35	31.39	41.37	39.95	27.43	26.18	21.71	150.21	125.45	127.98	125.29
<i>c</i>	77.34	50.75	27.19	34.43	31.35	41.59	40.20	28.44	25.78	21.77	150.29	125.86	128.30	125.63
<i>d</i>	82.24	52.39	27.80	35.65	33.14	42.74	40.88	23.67	30.18	21.94	153.91	127.09	129.76	126.81
<i>f</i>	78.04	48.70	27.01	35.02	32.97	42.66	40.67	31.33	21.46	21.84	150.55			
(2b)	76.44	50.26	26.38	34.32	31.29	41.37	39.53	23.84	28.99	21.72	151.22	125.33	128.06	125.42
<i>c</i>	76.39	50.56	26.76	34.47	31.28	41.59	39.80	25.49	27.99	21.79	151.13	125.78	128.36	125.71
<i>d</i>	81.02	52.01	27.35	35.46	32.85	42.66	40.59	21.67	31.66	21.93	154.25	127.01	129.90	127.11
(2c)	76.28	50.28	26.08	34.46	31.39	41.64	39.26	20.99	31.16	21.80	152.19	124.95	127.97	124.28
<i>e</i>	75.59	49.73	25.57	34.07	31.13	41.24	38.99	20.29	31.54	21.87	152.37	124.72	127.90	124.00
<i>c</i>	76.14	50.19	26.17	34.42	31.30	41.62	39.26	21.58	30.77	21.87	152.21	125.18	128.25	124.64
(2d)	75.76	50.29	27.29	34.35	31.32	41.89	40.25	30.76	23.33	21.80	149.08	125.77	127.69	125.15
<i>c</i>	76.29	50.97	27.57	34.72	31.42	42.27	40.61	31.42	23.99	21.95	149.44	126.31	127.86	125.53
(2e)	76.92	49.86	26.94	34.37	31.22	41.25	39.97	27.28	26.59	21.64	150.77	125.56	127.70	125.37
<i>c</i>	76.71	50.20	27.30	34.49	31.24	41.56	40.15	28.28	25.96	21.73	150.72	125.88	127.87	125.64
(2f)	77.15	49.97	27.10	34.41	31.29	41.29	39.99	27.90	25.77	21.68	150.58	125.41	127.82	125.34
<i>c</i>	76.93	50.42	27.43	34.57	31.35	41.67	40.25	29.07	25.11	21.82	150.53	125.98	128.08	125.65

^a CDCl₃, unless otherwise mentioned. ^b [2H₆]DMSO. ^c [2H₆]Benzene. ^d HFIP. ^e CDCl₃, temperature -20 °C. ^f Solid state.

measurements. Syntheses of the compounds are described elsewhere^{1b,8} N.m.r. data are in Tables 1 and 2 and in Supplementary Publication No. SUP 56692 (5 pp.).* The n.m.r. spectra for (1) in CDCl₃ solution depend on concentration. P_A becomes smaller at higher concentrations.

Crystal Structure Determination of (2a).—*M* = 364.483, monoclinic, space group *P*2₁, *a* = 11.516(1) Å, *b* = 10.190(5) Å, *c* = 9.886(1) Å, β = 114.12(1)°, *V* = 1 058.81 Å³, *Z* = 2, *D*_x = 1.143 g cm⁻³, λ(Cu-K_α) = 1.5418 Å, μ = 5.9 cm⁻¹, *F*(000) = 392, *T* = 293 K, final *R* = 0.040 for 1 897 observed independent reflections. Single crystals were prepared by recrystallization. *D*_m was not determined. The single crystal had dimensions ca. 0.43 × 0.17 × 0.25 mm. An Enraf-Nonius CAD4 diffractometer was used with graphite-monochromatized Cu-K_α radiation. Unit-cell parameters were chosen by least-squares refinement of the setting angles of 25 centred reflections with 2θ < 90°. An absorption correction was not applied. Intensities of reflections (*h* 0—14, *k* 0—12, *l* -12—12) with

sinθ/λ < 0.62 Å⁻¹ were measured at room temperature. Three reflections (512̄, 514̄, 525) were monitored after every 10⁵ s exposure time; loss in intensity in the total exposure time of 89 h was 5.2%. The *h*0*l* intensities were stronger than the other intensities.

Of 2 229 measured independent reflections, 1 897 with *I*_o > 3σ(*I*_o) were considered as observed with 332 unobserved. The structure was solved with direct methods, using MULTAN 11/82¹¹ implemented in the SDP system of Enraf-Nonius.¹² At first, problems were encountered because of the hypercentric distribution of the dominant *h*0*l* intensities. These problems were solved by independent normalization of the *h*0*l* and the other reflections. All non-hydrogen atoms were located, except C(10) which was found by subsequent difference Fourier synthesis. Hydrogen positions were calculated and confirmed in difference Fourier maps. Refinement by full-matrix least squares on |*F*| of the following parameters took place: positional and anisotropic thermal parameters of all non-hydrogen atoms, positional parameters of hydrogen atoms except H(16)—H(18) which were assumed as riding on C(10), and isotropic thermal parameters of all hydrogen atoms. Final positional parameters are given in Table 3.

* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1988, Issue 1.

Table 3. Positional parameters of (2a). Estimated standard deviations in parentheses

Atom	x	y	z
C(1)	-0.012 0(2)	0.183 3(2)	-0.043 5(2)
C(2)	-0.148 2(2)	0.233 9(2)	-0.092 8(2)
C(3)	-0.226 9(2)	0.166 4(3)	-0.240 7(3)
C(4)	-0.173 9(2)	0.183 3(4)	-0.356 6(3)
C(5)	-0.037 4(2)	0.133 5(3)	-0.303 5(3)
C(6)	0.042 1(2)	0.202 8(3)	-0.158 4(3)
C(7)	-0.208 4(2)	0.218 0(3)	0.022 8(2)
C(8)	-0.150 3(2)	0.315 2(4)	0.151 9(3)
C(9)	-0.187 4(2)	0.079 6(3)	0.088 2(3)
C(10)	0.018 5(2)	0.155 1(7)	-0.418 6(2)
C(11)	-0.350 6(2)	0.251 0(3)	-0.054 4(2)
C(12)	-0.445 7(2)	0.157 4(3)	-0.079 5(3)
C(13)	-0.573 4(2)	0.193 0(4)	-0.145 6(3)
C(14)	-0.609 4(2)	0.318 5(4)	-0.187 4(3)
C(15)	-0.516 6(2)	0.412 4(3)	-0.164 9(3)
C(16)	-0.389 1(2)	0.378 6(3)	-0.099 6(3)
O(17)	0.071 6(1)	0.256 2(2)	0.089 2(2)
C(18)	0.163 1(2)	0.191 1(3)	0.194 6(3)
O(19)	0.183 8(2)	0.076 1(2)	0.194 2(3)
C(20)	0.240 1(2)	0.279 8(3)	0.323 6(2)
O(21)	0.194 4(2)	0.313 8(3)	0.407 7(2)
C(22) ^a	0.367 8(2)	0.320	0.339 1(2)
C(23)	0.443 2(2)	0.393 9(4)	0.461 5(3)
C(24)	0.563 0(3)	0.433 5(4)	0.474 7(3)
C(25)	0.606 3(2)	0.401 3(4)	0.369 8(3)
C(26)	0.532 1(2)	0.329 1(4)	0.249 3(3)
C(27)	0.413 0(2)	0.287 7(3)	0.233 1(2)
H(1)	-0.009(2)	0.092(3)	-0.015(2)
H(2)	0.125(2)	0.174(3)	-0.121(3)
H(3)	0.038(3)	0.302(3)	-0.183(3)
H(4)	-0.043(2)	0.038(3)	-0.287(3)
H(5)	-0.236(2)	0.134(3)	-0.449(3)
H(6)	-0.183(3)	0.275(4)	-0.389(3)
H(7)	-0.241(2)	0.079(4)	-0.214(3)
H(8)	-0.314(2)	0.186(3)	-0.281(2)
H(9)	-0.151(2)	0.324(2)	-0.110(2)
H(10)	-0.196(3)	0.333(4)	0.200(3)
H(11)	-0.061(2)	0.299(4)	0.217(3)
H(12)	-0.147(3)	0.404(4)	0.101(4)
H(13)	-0.223(2)	0.068(4)	0.155(3)
H(14)	-0.211(2)	0.024(4)	0.007(3)
H(15)	-0.085(2)	0.073(4)	0.154(3)
H(16) ^b	-0.035	0.100	-0.521
H(17) ^b	0.008	0.276	-0.447
H(18) ^b	0.098	0.110	-0.376
H(19)	-0.421(2)	0.057(3)	-0.042(3)
H(20)	-0.643(3)	0.125(4)	-0.153(3)
H(21)	-0.701(2)	0.338(3)	-0.237(3)
H(22)	-0.542(2)	0.505(3)	-0.199(3)
H(23)	-0.330(2)	0.437(3)	-0.085(2)
H(24)	0.417(3)	0.429(4)	0.524(3)
H(25)	0.612(3)	0.473(5)	0.567(4)
H(26)	0.691(2)	0.424(3)	0.389(2)
H(27)	0.560(2)	0.316(4)	0.173(3)
H(28)	0.361(2)	0.233(3)	0.144(2)

^a No standard deviation calculated because the y co-ordinate of C(22) was fixed to define the origin. ^b No standard deviation calculated because atom was assumed as riding on C(10).

The refinement converged to a final $R = 0.040$ and $R_w = 0.053$, $S = 2.112$ ($S^2 = \text{G.o.f.}$). $(\Delta/\sigma)_{\text{max.}} = 0.13$ for 356 parameters with weighting function $w = 1/\sigma^2(F)$, where $\sigma^2(F) = (\sigma^2 + 0.04I)/4I$ with σ^2 from counting statistics. The final difference Fourier shows no significant features, the difference density values ranging between $+0.15$ and $-0.23 \text{ e}\text{\AA}^{-3}$. All calculations were carried out using the SDP program system.¹³ Atomic scattering factors and anomalous dispersion corrections were from refs. 13 and 14. Drawings were made by ORTEP.¹⁵

Acknowledgements

We thank Professor W. Steglich, Bonn, Professor H. Günther, Siegen, Dr. A. Jans, Brussels, and Professor R. Kosfeld, Duisberg, for n.m.r. measurements.

References

- (a) Part 2, H. Koch, H.-D. Scharf, J. Runsink, and H. Leismann, *Chem. Ber.*, 1985, **119**, 1485; (b) Part 3, A. Nehrings, H.-D. Scharf, and J. Runsink, *Angew. Chem.*, 1985, **97**, 882; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 877.
- (a) H. E. Ensley, C. A. Parnell, and E. J. Corey, *J. Org. Chem.*, 1978, **43**, 1610; (b) W. Oppolzer, *Angew. Chem.*, 1984, **96**, 840 and references cited therein on chiral Diels-Alder and ene reactions; (c) J. K. Whitesell, A. Bhattacharya, and K. Henke, *J. Chem. Soc., Chem. Commun.*, 1982, 988 (chiral Grignard reactions); (d) G. Quinkert, U. Schwartz, H. Stark, W. D. Weber, H. Baier, F. Adam, and G. Dürner, *Angew. Chem.*, 1980, **92**, 1062; (e) M. Newcamb, D. L. Turner, T. Kaneko, and D. E. Bergbreiter, *Tetrahedron Lett.*, 1979, 103 ('reversed' Prelog reactions); (f) P. Grossen, P. Herold, P. Mohr, and C. Tamm, *Helv. Chim. Acta*, 1984, **67**, 1625 (chiral homo-Aldol reaction).
- G. Helmchen, *Tetrahedron Lett.*, 1974, 1527.
- (a) R. Parthasarathy, J. Ohrt, A. Horeau, J. P. Vigneron, and H. B. Kagan, *Tetrahedron*, 1970, **26**, 4705; (b) J. M. Ohrt and R. Parthasarathy, *J. Cryst. Mol. Structure*, 1975, **5**, 359.
- D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, 1967, **89**, 5315.
- D. E. Woessner, B. S. Snowden, Jr., and G. H. Meyer, *J. Chem. Phys.*, 1969, **50**, 719.
- P. B. Koster, J. Runsink, and M. J. Janssen, *J. Chem. Soc., Perkin Trans. 2*, 1979, 393.
- C. W. Haigh and R. B. Mallion, *Org. Magn. Reson.*, 1972, **4**, 203.
- D. Seebach and V. Prelog, *Angew. Chem.*, 1982, **94**, 696.
- H. Koch, J. Runsink, and H.-D. Scharf, unpublished results.
- P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, Multan 11/82, A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, University of York, 1982.
- B. A. Frenz, Structure determination package, Enraf-Nonius, Delft, 1983.
- 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. IV.
- J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.
- C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.

Received 6th January 1986; Paper 6/049