EFFECTS ON THE N.M.R. SPECTRA OF THE STEREOCHEMISTRY OF 3,4-DIARYLADIPIC ESTERS AND 1,2-DIARYLCYCLOPENTANES[1]

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ABSTRACT

Examination of the n.m.r. spectra of *cis*- and *trans*-1,2-diphenylcyclopentane and 3,4-diphenylcyclopentanone substituted in the para positions of both rings with methoxyl, methyl, and chloro substituents has shown that the previous explanation (1) of the effect of temperature on the n.m.r. spectra of 1,2-diphenylcyclopentane and 3,4-diphenylcyclopentanone (unsubstituted) was incorrect. The n.m.r. spectra provide no evidence of restriction of rotation of the aromatic rings of these compounds. An alternative explanation is offered.

Comparison of the spectra of the compounds above and those of *meso*- and *dl*-3,4-diphenyladipic esters with the para substituents mentioned leads to the observation that in the *dl*-adipates and the *cis*-cyclopentanes the position of absorption of the protons ortho to the central structure (H_R) is shifted to higher field compared to the corresponding meso or trans isomer by an amount ranging from 0.2 to 0.7 p.p.m. The protons ortho to the substituent X (H_X) are also shifted to higher field but by only about 0.1 p.p.m.

Shifts of the benzylic protons of the *trans*-cyclopentanes and cyclopentanones to higher field amount to 0.3–0.6 p.p.m. in agreement with previous work (1, 34). The corresponding shift of the benzylic protons of the *meso*-adipic esters is only 0.1–0.2 p.p.m. The methylene protons and the methyl ester protons of the *meso*-adipates are also shifted to higher field by about 0.3 and 0.2 p.p.m. respectively.

These shifts seem adequately explained in terms of ring current effects of the benzene rings and lead to the possibility of obtaining detailed information concerning the stereochemistry of such substances. They are of immediate value in making configurational assignments to related compounds.

INTRODUCTION

In the course of an investigation (1) of the steric interaction of cis phenyl groups (relative to trans) in the 1,2-diphenylcyclopentanes I and a number of other related compounds it was observed that the nuclear magnetic resonance spectrum of *cis*-I, either without any solvent or in carbon tetrachloride, at room temperature showed the absorption attributable to the aromatic protons as two incompletely resolved broad sets of absorptions. Similar behavior was shown by *cis*-3,4-diphenylcyclopentanone *cis*-II, but the corresponding trans isomers and either *cis*- or *trans*-1,2-diphenylcyclopropane showed the narrow absorption to be expected by analogy with the aromatic proton spectrum of toluene (2). The aromatic proton spectrum of the *cis*-diphenylcyclopentanes narrowed on heating. Thus, the aromatic proton spectrum of *cis*-I with a bandwidth at half-height of 25 c.p.s. at 60 Mc sec at 25° had a bandwidth at half-height of 5 c.p.s. at 182°. It was proposed that the origin of the broadening in the *cis*-diphenylcyclopentanes *cis*-I and *cis*-II was due to restricted rotation of the phenyl rings with consequent non-equivalence of the "inside" and "outside" hydrogens. The present investigation of derivatives of *cis*- and *trans*-I, substituted in the para position, was undertaken to simplify and to make possible a more rigorous interpretation of the spectra. It has from the outset shown that the proposed explanation of the n.m.r. spectra of compounds such as *cis*-I in terms of restricted rotation of the phenyl rings is erroneous.

[1]*We are indebted to the Na ional Science Foundation (Grant G 14-480) for support of this work.*

EXPERIMENTAL[2]

Preparation of Materials

The compounds employed in the present investigation were either known compounds or close relatives of compounds which had already been prepared. Their physical properties and the syntheses employed are outlined in Table I. In addition to the para-substituted *cis*-1,2-diphenylcyclopentanes and *cis*-3,4-diphenylcyclopentanones originally sought a number of other compounds whose n.m.r. spectra are relevant to the present discussion are tabulated.

Nuclear Magnetic Resonance Spectral Determinations

Unless otherwise indicated n.m.r. spectra were obtained in deuterochloroform with tetramethylsilane as

TABLE IA

Physical properties of compounds studied

p-Substituent	Stereoisomer	M.p. of acid (° C)	Lit. m.p. (° C)	M.p. or [b.p.] of ester	Lit. value	Reference: Synthesis	Reference: Properties
		Methyl *trans*-cinnamates, X—$C_6H_4CH = CHCOOCH_3$					
CH_3O	—	—	—	89–90	89	3, 7	4
CH_3	—	—	—	57–57.5	57–58	7	6
Cl	—	—	—	75–76	75–76	6, 7	5
		Methyl hydrocinnamates, X—$C_6H_4CH_2CH_2COOCH_3$					
CH_3O	—	—	—	[278]	[278 at 1 atm]	10	9
HO	—	127–8	128–129	[195–197 at 16 mm]	[186–187 at 17 mm]	8, 12	8, 12
CH_3	—	120	120	[120–130 at 12 mm]	[132 at 20 mm]	12	8, 13
Cl	—	122	123	[145 at 8 mm]	*		14
		Dimethyl diaryladipates					
CH_3O	*meso*-IV	252–253	257–258	154–155	154.5–155.5 [165–185 at 0.5 mm]	7, 11	15, 16
	dl-IV	180–182	178–180	66–67 [235–237 at 2 mm]	63.5–64.5, 67 [235–250 at 0.8–1 mm]	7, 11	15, 16
HO	*meso*	326–328 (dec.)	†	215–216	‡	7, 13	—
	dl	224–225	§	147–148°	‖	7	—
CH_3	*meso*-VII	319–322	320	150–151	150	8	8
	dl-VII	200	—	Oil	—	8	—
H	*meso*	277–278	270–273	175–176°	177	7, 11	16
	dl	185–186	185–186	74.5–75.0	73–74	7, 11	16
Cl	*meso*-X	—	—	175	¶	8, 18	—
	dl-X	198–200	199–200	Oil [270 at 8 mm]	**	7, 8, 18	—
NO_2	*meso*	340 (d)	337–338(d)	243–244	234–235	7, 17	17
	dl	265	262–263	134–135	136–137	7, 17	17

*Found for the ester: C, 60.1; H, 5.5; Cl; 17.0. Calc. for $C_{10}H_{11}ClO_2$: C, 59.3; H, 5.5; Cl, 17.5.

†The same hydroxy acid was obtained both from the *meso*-methoxyphenyladipic acid by treatment for 50 minutes with 70 ml of 47 percent hydriodic acid and 10 ml of glacial acetic acid and from the *meso*-nitrophenyl acid by the method of ref. 17.

‡Found for the hydroxy ester: C, 66.5; H, 6.4. Calc. for $C_{20}H_{22}O_6$: C, 67.0; H, 6.2. The diacetyl derivative prepared from the hydroxy ester and acetyl chloride when recrystallized from ethanol had m.p. 175°. Found for $C_{24}H_{26}O_8$: C, 65.3; H, 6.0. Calc. for $C_{24}H_{26}O_8$: C, 65.2; H, 5.9.

§The *dl*-acid was prepared from the *dl*-dimethoxylphenyladipic acid by the hydriodic acid treatment employed for the meso isomer.

‖Found for the *dl*-ester: C, 66.6; H, 5.9. Calc. for $C_{20}H_{22}O_6$: C, 67.0; H, 6.2.

¶The meso ester was purified by recrystallization from methanol. Found: C, 60.6; H, 5.0; Cl, 17.9. Calc. for $C_{20}H_{20}Cl_2O_4$: C, 59.6; H, 5.0; Cl, 17.6.

**Found for the *dl*-ester: C, 59.3; H, 5.1; Cl, 17.5. Calc. for $C_{20}H_{20}Cl_2O_4$: C, 59.6; H, 5.0; Cl. 17.6.

[2]*All melting points are corrected and were determined with a microscope with a Koffler hot stage. Nuclear magnetic resonance spectra, unless otherwise indicated, were obtained by Mr. Dick Johnson and his associates. Microanalyses were provided by Mr. J. Nemeth and his associates.*

TABLE IB

Physical properties of compounds studied

p-Substituent	Stereoisomer	M.p. or [b.p.] (° C)	Lit. value	Reference: Synthesis	Reference: Properties
		3,4-Diarylcyclopentanones and [oximes]			
CH_3O	*cis*-VI	[oxime 124–125]	[oxime 124.5–125]	19	19
	cis-V*	[260–280 at 2–20 mm]			
	trans-V	111	110–111	19	19
	trans-VI	[oxime 127–128]	†		
CH_3	*cis*-VIII	80–82 [220–230 at 20 mm]	‡	19	—
	trans-VIII	102	§	19	—
H	*cis*-II	106	107	20	21
	trans-II	178–179	177	20	21
Cl	*cis*-XI	100	‖	19	—
	trans-XI	125–126	—	19	—
		1,2-Diarylcyclopentanes			
CH_3O	*cis*-III	56–57 [230–235 at 18 mm]	¶	22	23
	trans-III	72–72.5	**	22	—
CH_3COO		124.5	—	††	—
CH_3	*cis*-IX	[200–208 at 10–12 mm]	‡‡	22	—
	trans-IX	45.5	§§	22	—
		Other cyclopentanes			
p-Methoxyphenylcyclopentane		[149 at 22 mm]	[78–79 at 0.35 mm]	24	24
1,2-Bis-(*p*-methoxyphenyl)-cyclopentene		87–88	87.5–89	23	23

*Purified by distillation after recovery from the oxime (which had been chromatographed on alumina and recrystallized from benzene: ligroin 1:2) by hydrolysis with 4 *N* sulphuric acid containing a small amount of formaldehyde.

†Found for the oxime after recrystallization from benzene: ligroin 1:4: C, 73.3; H, 7.1; N, 4.0. Calc. for $C_{19}H_{21}NO_3$: C, 73.3; H, 6.8; N, 4.5.

‡Found for the *cis*-ketone after distillation and recrystallization from methanol: C, 86.4; H, 7.9. Calc. for $C_{19}H_{20}O$: C, 86.3; H, 7.6.

§Found for the *trans*-ketone after recrystallization from methanol: C, 86.4; H, 7.6. Calc. for $C_{19}H_{20}O$: C, 86.3; H, 7.6.

‖Found for the *cis*-ketone after recrystallization from chloroform – petroleum ether: C, 66.9; H, 4.6; Cl, 23.2. Calc. $C_{17}H_{16}Cl_2O$: C, 66.9; H, 4.6; Cl, 23.2.

¶A melting point of 56.5–57.5° has been reported (20) for an isomer of which the stereochemistry was not assigned. Found for the *cis*-cyclopentane after distillation and recrystallization from aqueous ethanol: C, 80.7; H, 8.0. Calc. for $C_{19}H_{22}O_2$: C, 80.8; H, 7.9.

**Found for the *trans*-cyclopentane after crystallization from ligroin: C, 80.0; H, 7.7. Calc. for $C_{19}H_{22}O_2$: C, 80.8; H, 7.9.

††Hydrolysis of *trans*-III by 2 hours of refluxing with 10 ml of acetic acid and 50 ml of 47% hydriodic acid gave a 67% yield of what was presumably the dihydroxyphenyl derivative, m.p. 173°, (recrystallized from carbon tetrachloride). The n.m.r. spectrum was in agreement with this structure. However, even at 100° under vacuum it apparently did not lose solvent imbedded in the crystal because the carbon analysis was 3.4% below that expected. The compound dissolved in dilute sodium hydroxide solution and when the basic solution was treated with acetic anhydride there resulted the diacetyl compound, m.p. 124.5° (recrystallized from ethanol). Found: C, 74.1; H, 6.5. Calc. for $C_{21}H_{22}O_4$: C, 74.5; H, 6.6. Hydrolysis of cis-III in the same way gave what was probably the *cis*-dihydroxy- compound, m.p. 72–73°.

‡‡Found after purification by distillation: C, 90.6; H, 9.0. Calc. for $C_{19}H_{22}$: C, 91.1; H, 8.9.

§§Found after crystallization from aqueous methanol: C, 90.9; H, 8.8. Calc. for $C_{19}H_{22}$: C, 91.1; H, 8.9.

an internal standard with a Varian A-60 spectrometer. As a check on the reliability of the instrument in the aromatic region, the absorption due to a trace of chloroform present in the deuterochloroform when it could be observed was found to be 2.75±0.05 p.p.m. Although the position of absorption of the chloroform proton is notoriously subject to shifts due to the interaction with other species present it appears that the values reported for the aromatic protons are reliable to about ±3 c.p.s. The n.m.r. results reported in τ units (25) are presented in Tables II, III, and IV.

DISCUSSION

Aromatic Proton n.m.r. Spectra

As will be seen from the data in Table IIIA the spectrum of the *cis*-di-*p*-methoxyphenylcyclopentane *cis*-III in deuterochloroform showed a single aromatic proton absorption in sharp contrast to the unsubstituted compound *cis*-I, which showed a broad

TABLE II

Positions of the aromatic protons in the n.m.r. spectra of monoaryl compounds, *meso*-diaryladipic esters and *trans*-diarylcyclopentanes

A. *para*-Methoxy compounds

Compound	Chemical shift (τ units)*			
	H_X	H_X(corr.)†	H_R	H_R(corr.)†
Methyl *p*-methoxyhydrocinnamate‡	3.16	3.17	2.86	2.87
p-Methoxyphenylcyclopentane	3.17	3.18	2.85	2.86
Dimethyl *meso*-di-(*p*-methoxyphenyl)-adipate (*meso*-IV)§	3.13	3.16	2.80	2.83
trans-Dimethoxyphenylcyclopentanone (*trans*-V)	3.18	3.19	2.94	2.95
trans-Dimethoxyphenylcyclopentanone oxime (*trans*-VI)	3.22	3.21	2.98	2.97
trans-Dimethoxyphenylcyclopentane (*trans*-III)‖	3.26	3.19	2.98	2.91¶
Range	3.19±0.07	3.18±0.03	2.89±0.09	2.90±0.07
p-Methoxytoluene (27)	3.20		2.95	

B. *para*-Methyl compounds

	$H_X \simeq H_R$	H(corr.)
Methyl *p*-methylhydrocinnamate	2.87	2.88
Dimethyl *meso*-di-(*p*-methylphenyl)-adipate (*meso*-VII)	2.80	2.84
trans-Di-(*p*-methylphenyl)-cyclopentanone (*trans*-VIII)	2.90	2.92
trans-Di-(*p*-methylphenyl)-cyclopentane (*trans*-IX)	2.97	2.85
Range	2.87±0.09	2.88±0.04
p-Methylisopropylbenzene (28)	2.92	

C. *para*-Chloro compounds

	H_X	H_X(corr.)	H_R	H_R(corr.)
Methyl *p*-chlorohydrocinnamate	2.66	2.77	2.76	2.87
Dimethyl *meso*-di-(*p*-chlorophenyl)-adipate (*meso*-X)	2.62	**	2.70	**
trans-Di-(*p*-chlorophenyl)-cyclopentanone (*trans*-XI)††	2.60	**	2.70	**
Range	2.63±0.03		2.73±0.03	
p-Chlorotoluene‡‡	2.73		2.83	

*Although, strictly speaking, the spectra are those of an A_2B_2 type they approximate the spectra to be expected of two independent AB systems superimposed as has been observed in previous studies (29) of *p*-disubstituted benzenes. Accordingly when the AB quartette was observed J and δ were calculated from the equation (30) $(1-3) = (2-4) = \sqrt{[(\delta_B-\delta_A)^2+J^2_{AB}]}$. In all cases where the spectrum was of this type, J, estimated as the separation between peaks 1 and 2 or 3 and 4, was found to be 9±0.5 c.p.s.

Spectra were obtained with 10–25% solutions (generally 20% in deuterochloroform unless otherwise specified. Spectra obtained in acetone agreed well with those in deuterochloroform, in general, and data obtained in acetone will be presented in footnotes to the Tables when they are available.

†The correction was applied by adding or subtracting the error estimated from a comparison of the position of the peak due to chloroform present as an impurity in the deuterochloroform with that of pure chloroform (2, p. 8), τ 2.73. The corrected values appear to have somewhat better internal consistency but the major conclusions are unaffected by the correction.

‡Methyl *p*-hydroxyhydrocinnamate (20% in acetone) had H_X 3.15, H_R 2.85 τ.

§In acetone (7%) dimethyl *meso*-di-(*p*-hydroxyphenyl-adipate had H_X 3.18, H_R 2.82 τ.

‖In acetone (20% solution) *trans*-III had H_X 3.27 and H_R 2.95. The analogous dihydroxyphenyl compound (20% in acetone) had H_X 3.28, H_R 3.00.

¶The spectrum of a neat sample showed H_X 3.71, H_R 2.81.

**No correction was possible since the chloroform peak was obscured by the aromatic absorption.

††The *trans*-ketone was obtained by the ring closure employed for the other *trans*-ketones in very small amount and not purified fully. The spectrum was obtained with a 4.8% solution in deuterochloroform.

‡‡In carbon tetrachloride the values were H_X 2.84, H_R 2.96. Although the positions of H_X and H_R of *p*-chlorotoluene have not been reported in a form which would make possible direct comparison with the present values their difference of 0.113 with H_R at higher field (29) agrees with the values here.

TABLE III

Positions of the aromatic protons in the n.m.r. spectra *dl*-diaryladipic esters and *cis*-diarylcyclopentanes

A. *para*-Methoxy compounds

Compound	Chemical shift (τ units)*			
	$H_X \simeq H_R$	H(corr.)	$(H_X^{dl} - H_X^{meso})$ or $(H_X^{cis} - H_X^{trans})$	$(H_R^{dl} - H_R^{meso})$ or $(H_R^{cis} - H_R^{trans})$
Dimethyl *dl*-di-(*p*-methoxyphenyl)-adipate (*dl*-IV)†	3.22†	3.25†	+0.09	+0.30
cis-Dimethoxy-phenylcyclopentanone (*cis*-V)‡	3.32	3.31	+0.12	+0.36
cis-Dimethoxyphen-ylcyclopentanone oxime (*cis*-VI)	3.27	3.28	+0.09	+0.33
cis-Dimethoxyphen-ylcyclopentane (*cis*-III)§	3.31	3.28	+0.09	+0.37
Range for the cyclopentane derivatives	3.29 ±0.03	3.29 ±0.02	+0.10 ±0.02	+0.35 ±0.02

B. *para*-Methyl compounds

	H_X	H_X(corr.)	H_R	H_R(corr.)		
Dimethyl di-(*p*-methylphenyl)-adipate (*dl*-VII)	2.92	2.88	3.14	3.10	0.00	+0.22
cis-Di-(*p*-meth-ylphenyl)-cyclo-pentanone (*cis*-VIII)	2.93	2.85	3.21	3.13	+0.01	+0.29
cis-Di-(*p*-methylphenyl)-cyclopentane (*cis*-IX)‖	3.08 3.11 (Av.) (3.10)	3.02 3.03 (3.03)	3.24 3.27 (3.26)	3.18 3.19 (3.19)	+0.06	+0.34
Range for the cyclopentane derivatives	2.97 ±0.4	2.94 ±0.09	3.23 ±0.04	3.16 ±.03	+0.03 ±.03	0.31 ±0.03

C. *para*-Chloro compounds

Methyl *dl*-di-(*p*-chlorophenyl)-adipate (*dl*-X)	2.75	2.79	3.09	3.13	+0.13¶	+0.39¶
cis-Di-(*p*-chlorophenyl)-cyclopentanone (*cis*-XI)	2.88	2.90	3.32	3.34	+0.28¶	+0.62¶

*The *J*'s had values from 8.5 to 9.0 c.p.s. Spectra were obtained with 10–25% solutions in deuterochloroform unless otherwise specified.

†8% solution in deuterochloroform. Dimethyl *dl*-(*p*-hydroxyphenyl)-adipate (15% solution in acetone) had H_A 3.11, H_B 3.25, for the aromatic proton absorption.

‡At −52° there was no noticeable change in the shape of the spectrum (determined by Mr. O. Norton) and $H_X = H_R$ was 3.37 (uncorrected). *cis*-3,4-(Dihydroxyphenyl)-cyclopentanone (20% acetone solution) had $H_X = H_R$ 3.37.

§A 16% solution of *cis*-III in acetone showed H_X and H_R at 3.23 and 3.43. In decalin (20% solution) at room temperature the corresponding values were 3.31 and 3.50. The separation between the peaks was essentially the same (12 c.p.s. between peaks 1 and 3) when the sample was heated to 180° as it was at room temperature (11 c.p.s. between peaks 1 and 3). The corresponding hydroxy compound had the aromatic chemical shifts at 3.33 and 3.45 in deuterochloroform and at 3.26 and 3.36 in acetone (20% solution). It will be noted that there is some possible ambiguity in making assignments of the H_X and H_R absorptions. They have been made here with the assumption that the H_X band is the lower one but without good justification.

‖A 20% solution of *cis*-IX in decalin showed H_X 3.25, H_R 3.37. On heating to 180° the two branches coalesced with $H_X = H_R$ 3.57. On recooling the AB quartette returned with H_X 3.11, H_R 3.27. The values of the chemical shifts in decalin were obtained with no calibration of the instrument in the region of interest and accordingly this result has only qualitative significance.

¶Since no corrected values could be obtained for the *meso-trans*-compounds, the uncorrected values were used throughout.

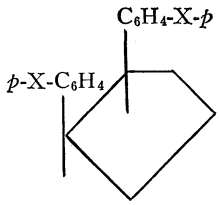
TABLE IV

Chemical shifts (τ units) of the aliphatic protons*

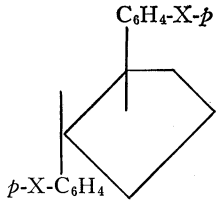
	Benzilic protons			Methylene protons			Ester protons		
p-Substituent or	meso (trans)	*dl* (cis)	*dl*−meso (cis−trans)	meso (trans)	*dl* (cis)	*dl*−meso (cis−trans)	meso (trans)	*dl* (cis)	*dl*−meso (cis−trans)
				A. Dimethyl diaryladipates					
CH_3O	6.72	6.63	−0.09	7.60	7.37	−0.23	6.60	6.42	−0.20
HO†	—	6.65	—	—	7.29	—	6.56	6.40	−0.16
CH_3	6.75	6.60	−0.15	7.58	7.33	−0.25	6.62	6.42	−0.20
H	6.69	6.51	−0.18	7.58	7.27	−0.31	6.63	6.41	−0.22
Cl	6.63	6.52	−0.11	7.58	7.29	−0.29	6.56	6.40	−0.16
NO‡	—	—	—	—	—	—	(6.59)	(6.40)	(−0.04)
Range	6.69 ±0.06	6.58 ±0.07	−0.14 ±0.05			−0.27 ±0.04			−0.19 ±0.03
				B. Cyclopentanones and oximes					
CH_3O	6.65	6.30	−0.35						
HO†	—	6.24	—						
CH_3	6.59	6.14	−0.45						
H	6.60 (6.52)	6.20 (6.17)	−0.40 (−0.45)§						
Cl	6.55	6.20	−0.35						
CH_3O	6.97	6.42	−0.55						
				C. Cyclopentanes					
CH_3O	7.04	6.67	−0.37						
CH_3	6.94	6.61	−0.33						
H	(7.00)	(6.68)	(−0.32)§						
CH_3COO	6.92	—	—						
Range	6.98 ±0.06	6.65 ±0.04	−0.44 ±0.12						

*Solvent deuterochloroform unless otherwise specified.
†Solvent acetone.
‡Solvent dimethylsulphoxide.
§Data from ref. (1) (solvent, carbon tetrachloride).

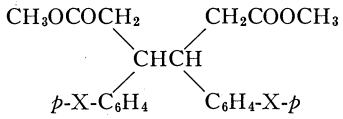
complex aromatic proton spectrum (1). (In acetone or decalin the aromatic proton spectrum of *cis*-III has the appearance of an AB spectrum (26) (doubled in this case) with a chemical shift between the A and B protons of 0.10–0.12 p.p.m.) This would seem at the outset not to be in accord with the previous postulation (1) of restricted rotation of the aromatic rings. In a further analysis of the n.m.r. data it is instructive first to consider together the spectra of those *p*-methoxy compounds which have only one phenyl ring and those which might be expected to have the maximum physical separation of the two phenyl rings and, hence, the minimum interaction of one phenyl ring with the other. Such a series, presented in Table IIA, includes, in addition to the compounds containing only one *p*-methoxyphenyl ring, the *meso*-dimethoxyphenyladipic ester (*meso*-IV) and the *trans*-dimethoxyphenylcyclopentane derivatives *trans*-III, *trans*-V, and *trans*-VI. The inclusion of the *meso*-adipic ester *meso*-IV is based on the somewhat intuitive premise to be discussed later that the predominate conformation is that (*meso*-A) with the aryl groups trans to each other, which places the CH_3OCOCH_2— groups trans to each other also. Each of these compounds had an aromatic proton spectrum which approximated the typical AB quartette as does *p*-methoxytoluene (27). The proton ortho to the substituent is designated by H_X; that ortho to the point of attachment of the molecule proper by H_R.



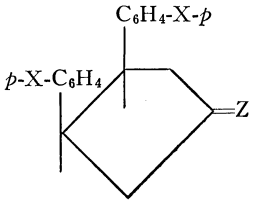
cis-I
cis-III
cis-IX



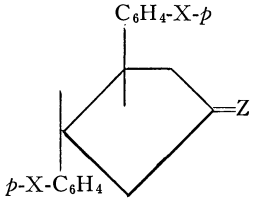
trans-I X = H
trans-III X = CH_3O
trans-IX X = CH_3



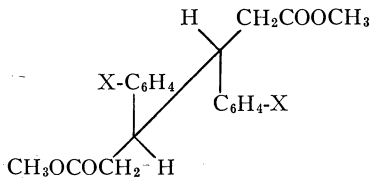
IV X = CH_3O
VII X = CH_3
X X = Cl



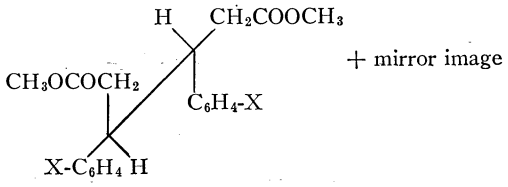
cis-II
cis-V
cis-VI
cis-VIII
cis-XI



trans-II X = H
trans-V X = CH_3O, Z = O
trans-VI X = CH_3O, Z = NOH
trans-VIII X = CH_3 Z = O
trans-XI X = Cl, Z = O



meso-A



dl-A

The data in Table IIA show the chemical shifts of the aromatic protons to be quite insensitive to changes in the carbon skeleton to which the benzene rings are attached. It can be seen further that the values for the two kinds of protons are scattered around the values of τ 3.20 and 2.95 for H_X and H_R obtained from the Varian Spectra Catalogue (27) for *p*-methoxytoluene. A similar situation exists in the *p*-methyl series (Table IIB) and also with the more limited and less dependable data available for the *p*-chloro series (Table IIC). Thus, the chemical shifts of H_X and H_R for the methyl compounds in Table IIB are sufficiently close to each other to appear as a single aromatic proton absorption close to the position of absorption (28) of *p*-methylisopropylbenzene.

In Table III are summarized the data for the aromatic proton spectra of the *dl*-diaryladipic esters and *cis*-diarylcyclopentane derivatives. The methoxy compounds (Table IIIA), in contrast to the meso–trans series, show, in deuterochloroform a single absorption attributable to both H_X and H_R. The methyl and chloro compounds (Tables IIIB and IIIC) have, as the aromatic proton spectrum, an AB quartette (28). As was the case with the series of Table II, the H_X (or H_R) values of the methoxy compounds (Table IIIA) are quite insensitive to the structural changes involved and this seems to be true also for the methyl compounds (Table IIIB) and chloro compounds (Table IIIC) although the data are rather limited. Most striking is the difference between the position of the H_X (or H_R) proton in the *dl*-cis series and that of the corresponding proton in the meso–trans

series. There is clearly a structural effect on the positions of the aromatic protons which is stereochemical in origin and which leads to a small shift to higher field (0.03–0.1 p.p.m.) of the H_X protons, in the *dl*–cis series and a somewhat larger shift (0.2–0.7 p.p.m.) again to higher field of the H_R protons. Although there is some indication that this difference is largest with the *p*-chloro compounds and smallest with the *p*-methyl the precision of the data is hardly adequate to justify any such correlation of the shift with the electrical effect of the substituent.

The shift to higher field of the aromatic protons of the compounds in the *dl*-cis series would seem to be primarily the result of the effect of the ring currents of each ring on the magnetic environment of the protons of the other adjacent to it. Such an effect was observed by Waugh and Fessenden (31) in their study of the paracyclophanes and in the series of *cis*-olefins and cyclic compounds (1, 30 p. 119 *ff.*) which led to the present investigation. It is of interest to compare the value of 0.57 p.p.m. for the shift to higher field relative to *p*-xylene of [2,2]paracyclophane (31) with the present data. Although it is not possible to make calculations with more than qualitative significance (32) because of the freedom to rotate of the phenyl rings in the diphenylcyclopentanes, inspection of molecular models makes it appear reasonable both that the shift of the paracyclophane should be comparable to those observed for H_R in the present examples and that shifts of H_R should be considerably larger than those of H_X.

The questions of the complexity and temperature dependence of the shape of the aromatic proton spectrum of the unsubstituted diphenylcyclopentane *cis*-I and the related diphenylcyclopentanone can now be considered. The results obtained with the *p*-substituted compounds just discussed explain readily the complexity of the spectra since the position of absorption of the ortho protons could be expected to be shifted more to higher field than the meta or para by the adjacent ring. Although the spectra of the unsubstituted compounds are too complex to permit assignments of chemical shift values to the ortho, meta, and para protons, the separation previously observed (1) between the centers of the two multiplets (0.2–0.3 p.p.m.) is of the order of magnitude expected from the study of the para-substituted relatives in Tables II and III.

A possibility which might be considered is that although rotation of the aromatic rings in the diphenyl compounds without para substituents is slow (on the n.m.r. time scale) it is accelerated by an electronic effect (which might alter the effective size of the π-electron cloud) of the para substituents. Substituents of the compounds studied include the methoxyl group with σ_{meta} negative, σ_{para} positive; the methyl group with σ_{meta} and σ_{para} both negative; and the chlorine atom with both σ_{meta} and σ_{para} positive. Since in none of these para-substituted compounds has there been complexity in the aromatic proton spectrum beyond that to be expected in molecules with freely rotating phenyl rings, such an explanation appears to be ruled out. As was noted in Table IIIA an attempt to slow the rotation of the *p*-methoxyphenyl rings of *cis*-III by cooling the solution to −52° made no significant change in the spectrum. It is anticipated that at lower temperatures or with appropriate ortho or meta substituents on the phenyl rings their rotation rates may be measured with n.m.r. techniques.

The most probable explanation of the narrowing at 180° (1)[3] of the phenyl proton spectrum in the cis compounds *cis*-I and *cis*-II appears to involve the non-coplanarity of the cyclopentane ring (33). Suppose, for example, that a solution of the *cis*-hydrocarbon *cis*-I contains at room temperature a mixture of molecules in two or more conformations

[3]*The examination of the n.m.r. spectrum of cis*-I *in decalin at room temperature and at 180° has been repeated with complete confirmation of the previous results (1).*

of the cyclopentane ring, which differ in the relative positions of the phenyl groups with respect to each other and which are in rapid equilibrium. The effective magnetic field at each H_R is then a weighted average which depends on the field at that proton in each of the conformations and on the equilibrium constant (s) describing the degree to which each conformation is populated. If the increase in temperature were to increase the populations of conformations in which the phenyl groups were most separated there would then be a preferential shift to lower field of the resonance position of the H_R protons and a corresponding narrowing of the proton resonance band.[4] This leads to the prediction that there should be a preferential shift to lower field of the H_R protons in the *cis*-1,2-diphenylcyclopentane derivatives. A compound which might be expected to show this effect most dramatically is the *para*-methyl compound *cis*-X, which was studied as a 20% solution in decalin. At room temperature as mentioned in the footnote to Table IIIB the AB quartette had a chemical shift between H_X and H_R of 0.12 p.p.m. At 180° the quartette had a single peak, in agreement with expectation. The *para*-methoxy compound *cis*-III (20% solution) in decalin failed to show a significant change in the shape of the aromatic proton spectrum. As was noted in Table IIIA, this substance, in contrast to its behavior in deuterochloroform, shows an AB quartette with a chemical shift between H_X and H_R of about 0.19 p.p.m. This separation did not change appreciably on heating. It seems clear that a detailed understanding of the temperature dependence of *cis*-diarylcyclopentanes awaits the accumulation of further experimental data. The difference between the spectra of deuterochloroform and acetone or decalin solutions in the cis series indicates that part of the chemical shift differences considered above between the cis–*dl* and trans–meso series is due to solvent interactions which are probably most serious with the deuterochloroform solutions (34).

Absorption of the Benzylic Protons

It was pointed out previously (1, 35) that a few *vic*-diphenylcyclic compounds and the stilbenes had a shift of the benzylic proton 0.32–0.50 p.p.m. to higher field in the trans isomer (in which the benzylic proton is cis to the phenyl ring on the adjacent carbon). In Tables IVB and IVC are presented data showing the benzylic proton absorptions of compounds now available. The value given is the center of the unresolved multiplet. Both the previous generalization relating configuration with benzylic proton absorption and the configurational assignments of the compounds in Tables IVB and IVC are confirmed with the benzylic protons of the trans isomers absorbing 0.44 ± 0.11 p.p.m. higher than the corresponding protons of the cis isomers.

Conformations of the Diphenyl Adipic Esters

It is of interest to compare more fully the n.m.r. spectra of the *meso*- and *dl*-adipic esters. At the outset it might be supposed that the staggered conformation in which the small hydrogen atom lies between the two larger groups on the adjacent carbon atom, as in *meso*- and *dl*-A, is the most populated one in each case. As a beginning then it is instructive to examine the positions of the proton resonances with the assumption that the meso isomers have the conformation *meso*-A, and that the *dl*-isomers have those shown as *dl*-A. On this basis it has already been noted (Table II) that the phenyl proton positions of the *meso*-adipic esters (with a dihedral angle of 180° between the bonds to the phenyl rings) are the same to within the present limits of the experimental measurement as those

[4]*Substantially this explanation was proposed by Dr. F. A. L. Anet, to whom we are indebted, in a letter written in April, 1962, before the results with the para-substituted compounds were available.*

of the *trans*-diarylcyclopentanones and cyclopentanes with a dihedral angle of 120°, neglecting the twisting of the five-membered ring.

The data in Table III might be interpreted as showing that the phenyl proton positions are not shifted quite as much to higher field in the *dl*-adipic esters (dihedral angle 60° as in conformation *dl*-IVA) as they are in the *cis*-cyclopentanes (dihedral angle nearly 0°). The precision of these data is not sufficient to permit more than a suggestion that this difference may be real. In any case the trend is reasonable, the greatest shift to higher field occurring with the smallest dihedral angle between the bonds to the phenyl rings. If the postulated conformations *meso*-A and *dl*-A are interpreted literally with the benzylic proton on one carbon atom centered between the bonds to the phenyl and methylene groups on the adjacent carbon atom, then the spacial relationship of the benzylic proton to the two aromatic rings is the same in the two conformations and there should be no shift due to a change in the effect of ring currents on the proton's environment. Data in Table IVA show that this prediction is not verified. The benzylic protons in the meso series are consistently somewhat higher (0.14 ± 0.05 p.p.m.) than the corresponding protons in the *dl*-series.[5] An improved picture would take into account the possibility that the stabilities of conformations *meso*- and *dl*-A can be increased by distorting them slightly so that the proton is not equidistant from the two bonds opposite it, and also the probable existence of an appreciable fraction of the molecules in the other staggered conformations, as well as the non-planarity of the cyclopentane ring. This over-simplified picture is of value, however, in a consideration of the shifts of the methylene protons and ester methyl protons (Table IVA). It is seen that the meso isomers which had the H_R protons at lower field (relative to the *dl*) have both the methylene and methyl protons shifted to higher field. This is readily explained if conformations *meso*-A and *dl*-A are assumed to be the most important conformations, since in *meso*-A the methylene and methyl ester groups are above the face of the opposite benzene ring and therefore subject to a ring-current shift to higher field. In the *dl*-isomer (conformation *dl*-A) the phenyl groups are adjacent.

It seems clear that with more refined data, n.m.r. studies are capable of giving detailed structural information about positions of conformational equilibria in systems such as the diphenyladipic esters. Hyne (36) has reported such studies of the diastereoisomeric ephedrines. In any case the positions in the n.m.r. spectrum of the H_R protons together with the methylene and methyl protons appears to provide a reliable method of assigning configuration to compounds similar to those studied here.

REFERENCES

1. D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer. J. Am. Chem. Soc. **83**, 4838. (1961); **84**, 863 (1962).
2. Varian Spectra Catalogue. Varian Associates, Palo Alto, Cal. 1962. Spectrum No. 157.
3. R. K. Callow, J. M. Gulland, and R. D. Haworth. J. Chem. Soc. 1444 (1929).
4. G. R. Ramage and R. Robinson. J. Chem. Soc. 607 (1933).

[5] *Another basis on which to make a comparison is to consider the chemical shift in relation to the approximate dihedral angle between the* C—*phenyl and* C—H *bonds on adjacent carbon atoms. Data for the two series available*

Series	*Dihedral angle) (approximate*	*Chemical shift* X═CH_3O	(τ) CH_3
cis-Cyclopentane	*120°*	*6.67*	*6.61*
dl-Diphenyladipate	*60°*	*6.63*	*6.60*
meso-Diphenyladipate	*60°*	*6.72*	*6.75*
trans-Cyclopentane	*0°*	*7.04*	*6.94*

in deuterochloroform (shown here) suggest that the dl-shifts fall quite close to the cis with the meso-adipates somewhat larger. The differences are too small to permit further analysis.

5. G. P. Scott. J. Org. Chem. **20**, 736 (1935).
6. K. C. Pandya and R. B. Pandya. Proc. Indian Acad. Sci. **14A**, 112 (1941).
7. T. Posner and G. Schreiber. Ber. **57**, 1127 (1924).
8. G. R. Ramage. J. Chem. Soc. 397 (1938).
9. W. Körner and P. Corbetta. Ber. **7**, 1731 (1874).
10. C. Paal and J. Gerum. Ber. **41**, 2273 (1908).
11. E. Bowden and H. Adkins. J. Am. Chem. Soc. **62**, 2422 (1940).
12. E. Fischer and O. Nouri. Ber. **50**, 611 (1917).
13. T. Koreber. Ber. **23**, 1033 (1890).
14. K. Kindler. Ann. **452**, 111 (1927).
15. C. L. Wilson and K. B. Wilson. Trans. Electrochem. Soc. **84**, 153 (1943).
16. A. L. Wilds and R. E. Sutton. J. Org. Chem. **16**, 1371 (1951).
17. H. E. Fierz-David, L. Blangey, and M. Uhlig. Helv. Chim. Acta, **32**, 1414 (1949).
18. I. Vogel. J. Chem. Soc. 594 (1927).
19. G. P. Mueller and F. C. Bateman. J. Am. Chem. Soc. **74**, 3959 (1952).
20. K. Bernhauer and R. Hoffmann. J. Prakt. Chem. **149**, 319 (1937).
21. H. A. Weildlich. Ber. **71B**, 1601 (1938).
22. H. Burton and C. W. Shoppee. J. Chem. Soc. 570 (1939).
23. G. P. Mueller, J. G. Fleckenstein, and W. H. Tallent. J. Am. Chem. Soc. **73**, 2651 (1951).
24. R. R. Burtner and J. M. Brown. J. Am. Chem. Soc. **75**, 2334 (1953).
25. G. v.D. Tiers. J. Phys. Chem. **62**, 1151 (1958).
26. J. A. Pople, W. G. Schneider, and H. J. Bernstein. High resolution nuclear magnetic resonance. McGraw-Hill Book Co., New York. 1959. p. 119 ff.
27. Varian Spectra Catalogue. Varian Associates, Palo Alto, Cal. 1962. Spectrum No. 205.
28. Varian Spectra Catalogue. Varian Associates, Palo Alto, Cal. 1962. Spectrum No. 268.
29. R. E. Klinck and J. B. Stothers. Can J. Chem. **40**, 2329 (1962). See also R. E. Richards and T. P. Schaefer. Trans. Faraday Soc. **54**, 1280 (1958); P. F. Cox. J. Am. Chem. Soc. **85**, 381 (1963) and references therein cited.
30. L. M. Jackman. Applications of nuclear magnetic resonance spectroscopy in organic chemistry. Pergamon Press, New York. 1959. pp. 89–90. J. J. Drysdale and W. D. Phillips. J. Am. Chem. Soc. **79**, 319 (1957).
31. J. S. Waugh and R. W. Fessenden. J. Am. Chem. Soc. **79**, 846 (1957).
32. C. E. Johnson and F. A. Bovey. J. Chem. Phys. **29**, 1012 (1958).
33. E. L. Eliel. Stereochemistry of carbon compounds. McGraw-Hill Book Co., New York. 1962. p. 248 ff.
34. J. A. Pople, W. G. Schneider, and H. J. Bernstein. High resolution nuclear magnetic resonance. McGraw-Hill Book Co., New York. 1959. p. 428 ff. See also R. Kaiser. Can. J. Chem. **41**, 430 (1963).
35. D. Y. Curtin, H. Gruen, and B. A. Shoulders. Chem. Ind. 1205 (1958).
36. J. B. Hyne. Can. J. Chem. **39**, 2536 (1961).