Conformational Preferences of Bridged Aromatic Compounds. II. Substituted Dibenzylbenzenes[1]

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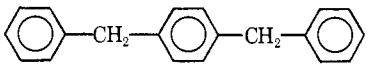
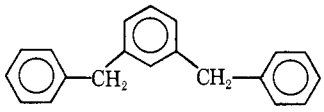
Abstract: Dipole moments and nmr data are reported for a series of substituted dibenzylbenzenes. It has been found that in *p*-dibenzylbenzenes (I) ortho substituents may induce conformational preferences so that cis and/or trans forms become preferred, according to the substitution pattern. The molecular shape of *m*- (II) and *o*-dibenzylbenzenes (III) is also influenced by ortho substitution and some preferred conformations have been detected.

Our study of the conformational properties of substituted diarylmethanes in solution[1,2] has been extended to some dibenzylbenzenes in order to investigate how ortho substitution, inducing conformational preferences, can influence the shape of these molecules.

The different molecular geometries of *p*- (I), *m*- (II), and *o*- (III) dibenzylbenzenes cause differences in the degree of steric restriction imposed on the rotation about the four torsional angles (IV).



I



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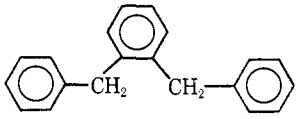

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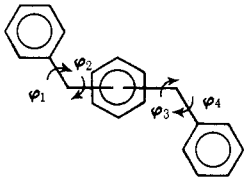


IV

In the para isomer I, the two phenyl rings attached to the central one never come close enough to each other to interact sensibly. This predictably will not be the case of ortho isomer III, in which the two side phenyl rings may easily come in close contact, generating steric repulsion. Accordingly, different conformational preferences are expected to arise in the three systems considered (ortho, meta, and para). Our results show that ortho substituents may cause cis and/or trans forms to become preferred, according to the substitution pattern.

Although both nmr and dipole moment measurements were undertaken by us, the bulk of our evidence on the conformational preferences comes from the nmr studies. Dipole moments proved by far less conclusive. However, once the conformational preference was established by nmr, dipole moment data were useful to get additional and/or complementary information.

(1) For a preliminary communication, see G. Montaudo, S. Caccamese, P. Finocchiaro, and F. Bottino, *Tetrahedron Lett.*, 877 (1970).

(2) See the preceding paper, G. Montaudo, S. Caccamese, and P. Finocchiaro, *J. Amer. Chem. Soc.*, **93**, 4202 (1971).

p-Dibenzylbenzenes

We have investigated only symmetrically substituted molecules. Neglecting the nature of the substituent, there are eight types of symmetrical ortho-substituted *p*-dibenzylbenzenes (Figure 1).

In Table I are reported the nmr chemical shifts of ortho methyl groups and ortho aromatic protons for a number of these compounds; chemical shifts of para nuclear hydrogens are also reported for comparison. In Table II are collected the dipole moment data for a number of appropriate halogen derivatives.

The chemical-shift behavior reproduces closely that observed for diphenylmethanes with identical substitution patterns at a single methylene bridge.[2] Since these effects have been discussed in the preceding paper,[2] no further explanation is needed here.

It may be noted that the information coming from diphenylmethane work is limited only to the conformation assumed by two aromatic rings in the molecule. In dibenzylbenzenes there are three aromatic rings and the conformational problem is about the shape of the overall molecule, *i.e.*, the relative spatial position (cis or trans) of the side rings.

Compounds of type X (**15–17**, **18**) and XI (**19–21**) both carry six ortho substituents, three around each methylene bridge. Nmr data in Table I indicate in both cases a strong preferential shielding (about 0.6 ppm) of the remaining ortho nuclear hydrogens. In Figure 2 is shown the nmr spectrum of compound **21** (type XI). This shielding strongly suggests that compounds of type XI exist predominantly in form XIa (trans), where the *two* ortho aromatic hydrogens lie below the adjacent ring. In fact, this is the only conformation in which *two* ortho nuclear hydrogens appear diamagnetically shielded from the adjacent aromatic rings.[3] Compound **21** in form XIa should have a resultant dipole moment of about 0 D. The experimental value of 0.94 D (Table II) forces one to conclude that some torsional oscillations are occurring around the equilibrium dihedral angle with consequent increase of the dipole moment value.[5]

(3) The theoretical shielding value calculated for conformer XIa through the Johnson and Bovey tables[4] is about 0.8 ppm, as inferred from inspection of the contour map in Figure 6 of the preceding paper.[2]

(4) C. F. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(5) Dipole moment data suggest here that some flipping of the phenyl rings occurs, while the magnitude of the diamagnetic shielding for the ortho nuclear hydrogens (0.6 ppm) compares well with those reported in the preceding paper[2] for tri-ortho-substituted compounds. This supports the view that all these shieldings represent time-averaged values.

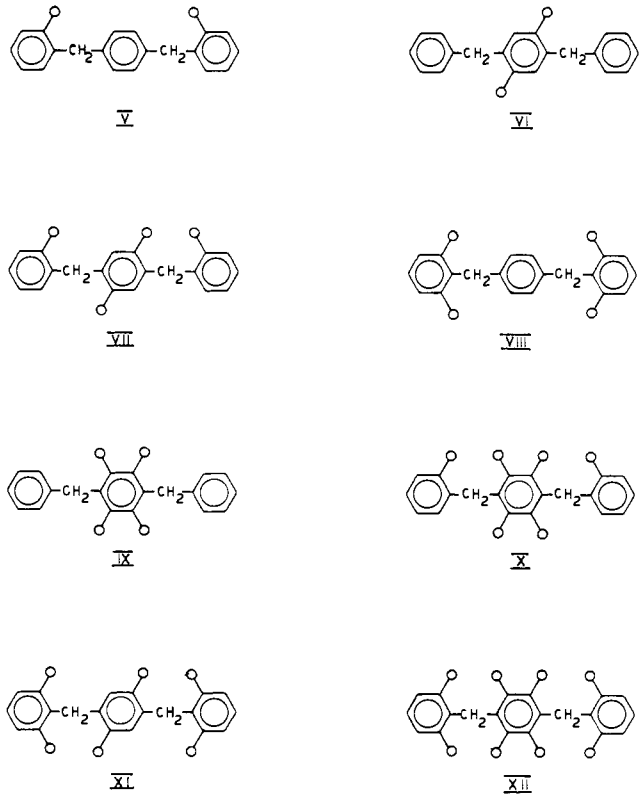
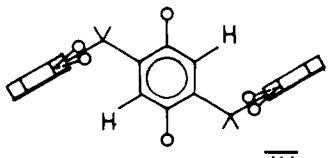


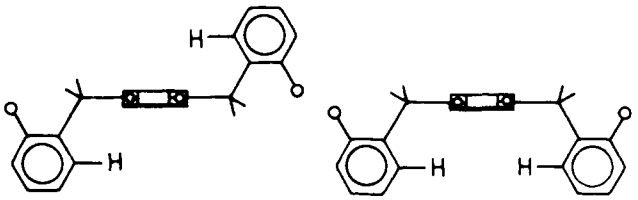
Figure 1. The symmetrical ortho-substituted *p*-dibenzylbenzenes.

In compounds of type X the preponderance of form XIa becomes unlikely due to the presence of four methyls in the central ring. Instead, in agreement with



XIa

the nmr data (Table I), two conformers (Xa and Xb) in which both ortho aromatic hydrogens lie below the central ring appear to be preferred.[6] The experimental dipole moment value for compound **18** (Table II) is lower than the value calculated for completely thermodynamically unrestricted rotation, but it is almost coincident with the value calculated (1.5 D) when forms Xa and Xb are considered present in equal amounts.



Xa Xb

For compounds of type VII (**5–7**) nmr data (Table I, Figure 3) show a certain degree of diamagnetic shielding

(6) In contrast to XIa, forms Xa and Xb are represented with the central ring perpendicular to the plane of the paper. This reflects the fact that in form XIa the central ring lies in the plane containing the four C_{Ar}–C bonds while in forms Xa and Xb the side rings are contained in the above plane and the central ring is perpendicular to it.

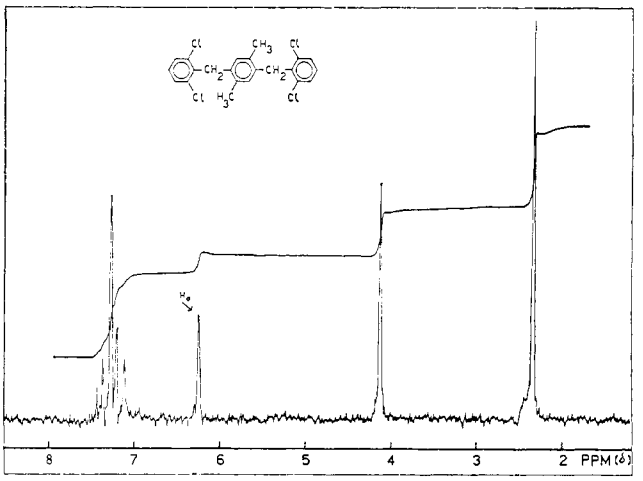


Figure 2. Nmr spectrum of compound **21**. The label H_o denotes the peak due to the shielded ortho protons.

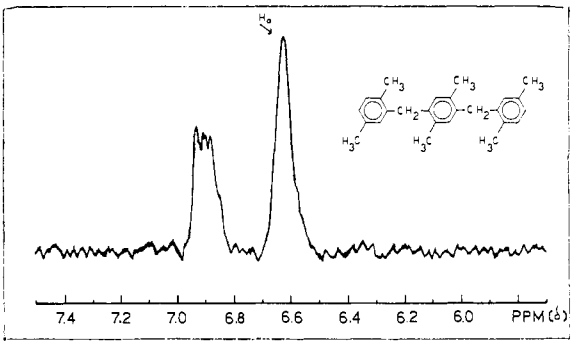


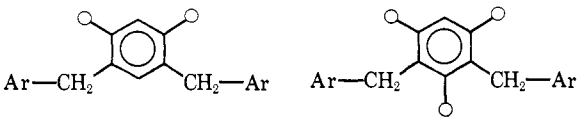
Figure 3. Nmr spectrum (aromatic region) of compound **6**. The label H_o denotes the peak due to the shielded ortho protons.

(about 0.2 ppm) for all the ortho nuclear hydrogens, suggesting that these molecules exist in a preferred skew conformation[2] (cis and trans). The experimental dipole moment value (**7**, Table II), however, is inconclusive for the detection of this conformational preference. In analogy with identically substituted diphenylmethanes,[3] the molecule may be thought to be undergoing some torsional oscillations about the equilibrium dihedral angle with consequent averaging of the dipole moment value, which becomes close to that calculated for the thermodynamically unrestricted rotation.

Data in Tables I and II for compounds of type V (**1–3**), VI (**4**), VIII (**8–11**), IX (**12–14**), and XII (**22–24**) come very close to those expected for a thermodynamically unrestricted rotation. These results, however, do not necessarily rule out that some of these compounds (*i.e.*, type XII) exist preferentially in rapidly interconverting skew forms (cis and trans) for which averaging in the nmr signals must occur.

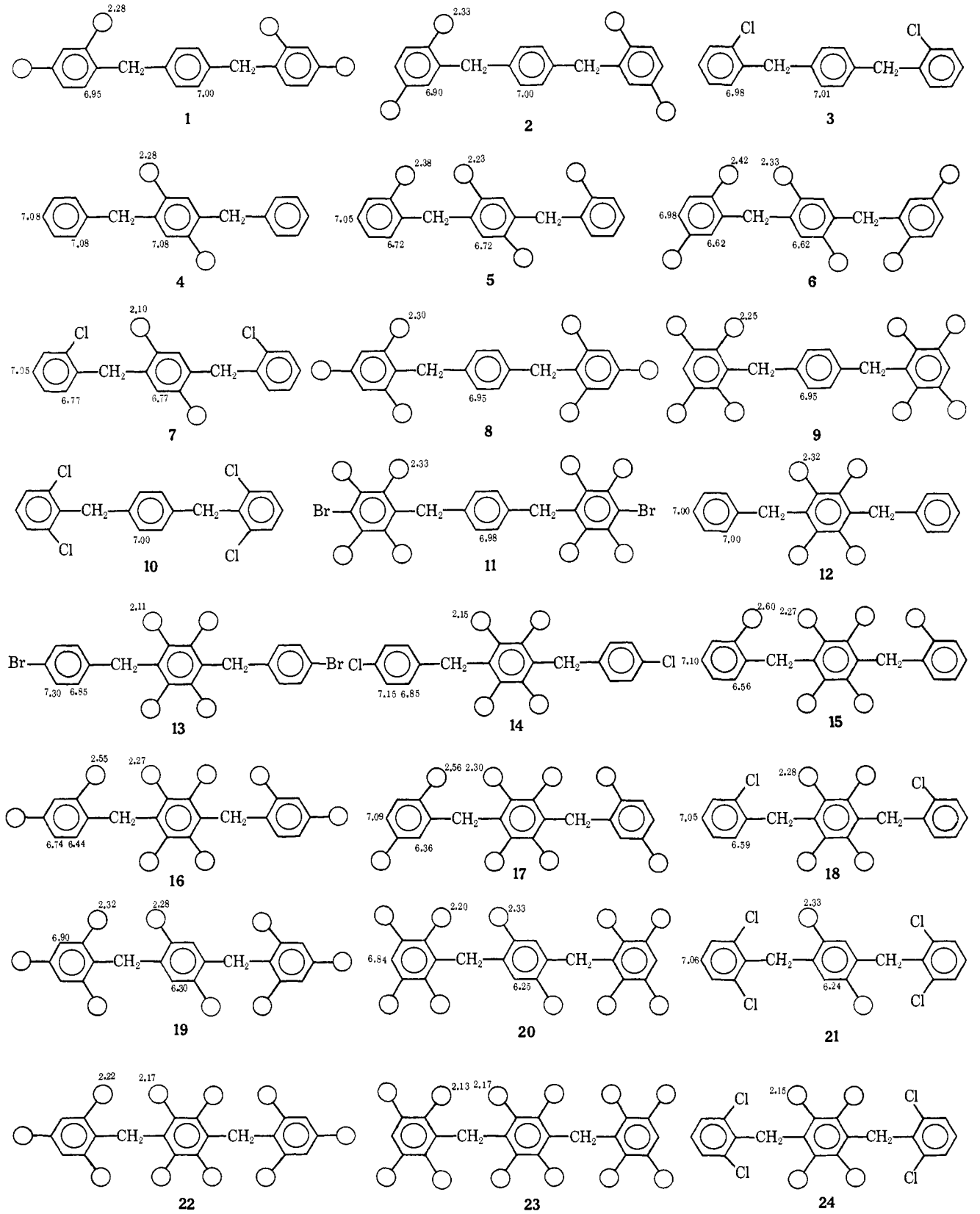
m-Dibenzylbenzenes

Data in Table III relating to the nmr chemical shifts of ortho methyl groups and ortho aromatic protons are limited to only two types of substituted *m*-dibenzylbenzenes (XIII and XIV).



XIII XIV

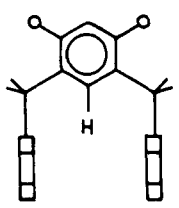
Table I. Chemical Shifts[a] of Relevant Groups (○ = CH_3) in *p*-Dibenzylbenzenes



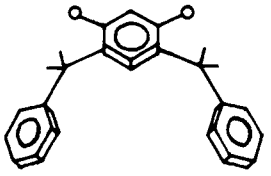
[a] Chemical shifts measured in $CDCl_3$ at 30°, in parts per million downfield from TMS as internal standard (60 MHz).

Excluding conformations in which all the aromatic rings are coplanar,[2] two lower energy forms (*inter alia*) can be written for compounds of type XIII (**25–30**).

Nmr data (Table III) show that ortho substitution shifts the conformational equilibrium in favor of the form XIIIa. This is particularly true in the case of compounds **28–30** and, to a lesser extent, of compounds **26** and **27**.



XIII a



XIII b

In fact, form XIIIa is the only one in which an ortho nuclear proton is expected to be diamagnetically shielded by the two side rings. As shown in Table III and Figure 4 (**29**) the shielding (1.51 ppm) is actually doubled with respect to previous cases (*i.e.*, see Figure 2).

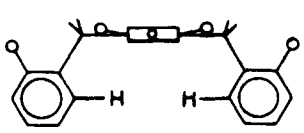
Table II. Experimental and Calculated Values of the Dipole Moments of Substituted *p*-Dibenzylbenzenes

Compd	Exptl	Calcd: Free rotation	Calcd: Cis	Calcd: Trans
11	1.99	2.32	3.28	0
13	2.09	2.32	3.28	0
14	2.10	2.34	3.31	0
10	1.60	1.42	2.01	0
21	0.94	1.42	2.01	0
24	1.44	1.42	2.01	0
3	2.17	2.01	2.09[a]	1.93[b]
7	2.02	2.01	2.09[a]	1.93[b]
18	1.43	2.01	2.16[c]	0[d]

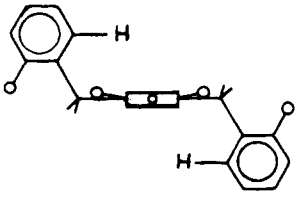
[a] Calculated for the cis form with thermodynamically unrestricted rotation about φ_1 and φ_2 (IV). [b] Calculated for the trans form with thermodynamically unrestricted rotation about φ_1 and φ_2 (IV). [c] Calculated for form Xb. [d] Calculated for form Xa.

A theoretical shielding value of about *1.6 ppm* is calculated[4] for the nuclear proton between the two side phenyl rings in form XIIIa by means of the contour map given in the preceding paper (Figure 6[2]) and assuming independent contributions for each phenyl group. In addition, form XIIIa accounts correctly also for the deshielding experienced by the ortho methyl groups in the central ring.

In compounds of type XIV (**31–34**), where a bulky methyl group replaces the hydrogen atom between the two side rings, form XIIIa cannot be the preferred one. Nmr data (Table III) suggest that two conformers (XIVa, XIVb) become preferred, when one ortho methyl group per side phenyl ring is present. In fact, the two aromatic hydrogens which lie below the central ring experience a diamagnetic shielding of about 0.5–0.6 ppm and ortho methyl groups of the side rings appear deshielded, as expected.



XIV a



XIV b

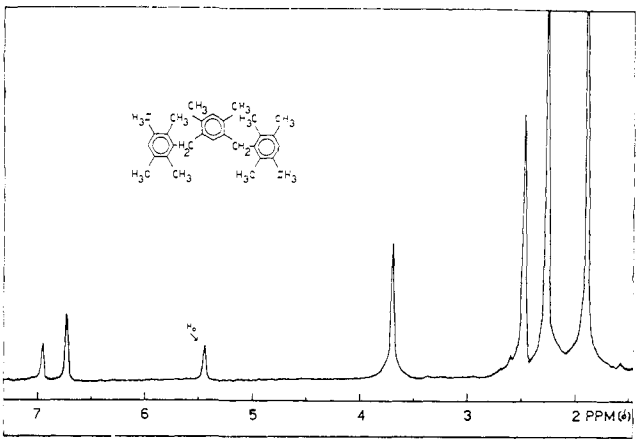
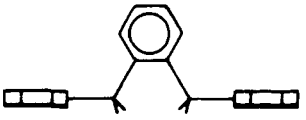


Figure 4. Nmr spectrum of compound **29**. The label H_o denotes the peak due to the shielded ortho proton.

For compound **34**, where all eight ortho positions around the two methylene bridges are substituted, methyl signals are found at average field values, reproducing a situation already described.

o-Dibenzylbenzenes

In Table IV are collected the nmr chemical shifts of ortho methyl groups and shifts referring to the aromatic protons of the central ring, for a series of *o*-dibenzylbenzenes. In the case of *o*-dibenzylbenzenes, the conformer XV might be thought to be somewhat preferred even in the unsubstituted molecule (III).



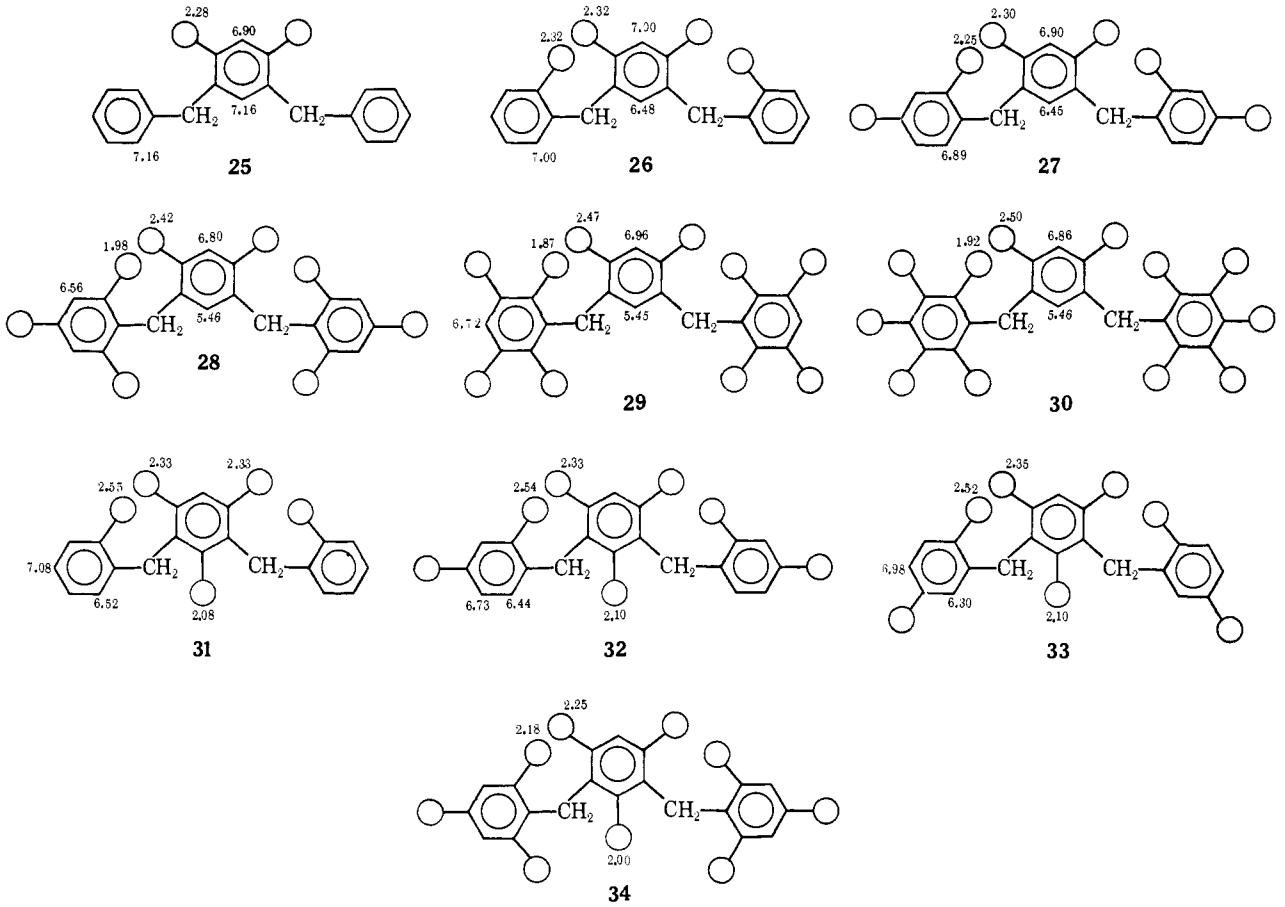
XV

However, one should allow for some torsional oscillations to take place around the equilibrium dihedral angle (involving twist angles φ_2 and φ_3, IV), while the rotation around φ_1 and φ_4 can be considered thermodynamically almost unrestricted. Under these conditions, no preferential shielding of the ortho aromatic protons may be predicted for the unsubstituted molecule, as experimentally found (**35**, Table IV).

Ortho methyl substitution in the side rings greatly increases the steric hindrance to internal rotation, so that conformer XV becomes strongly preferred in compounds **38–41**, as shown by data in Table IV. In fact, a chemical-shift difference of about 0.35 ppm is found between protons (central ring) ortho and meta with respect to the methylene bridges. A theoretical shielding value of about 0.6 ppm is calculated[4] in this case. The relatively poor agreement with the experimental value may be partly due, in this case, to the difficulty of choosing unperturbed protons for reference.

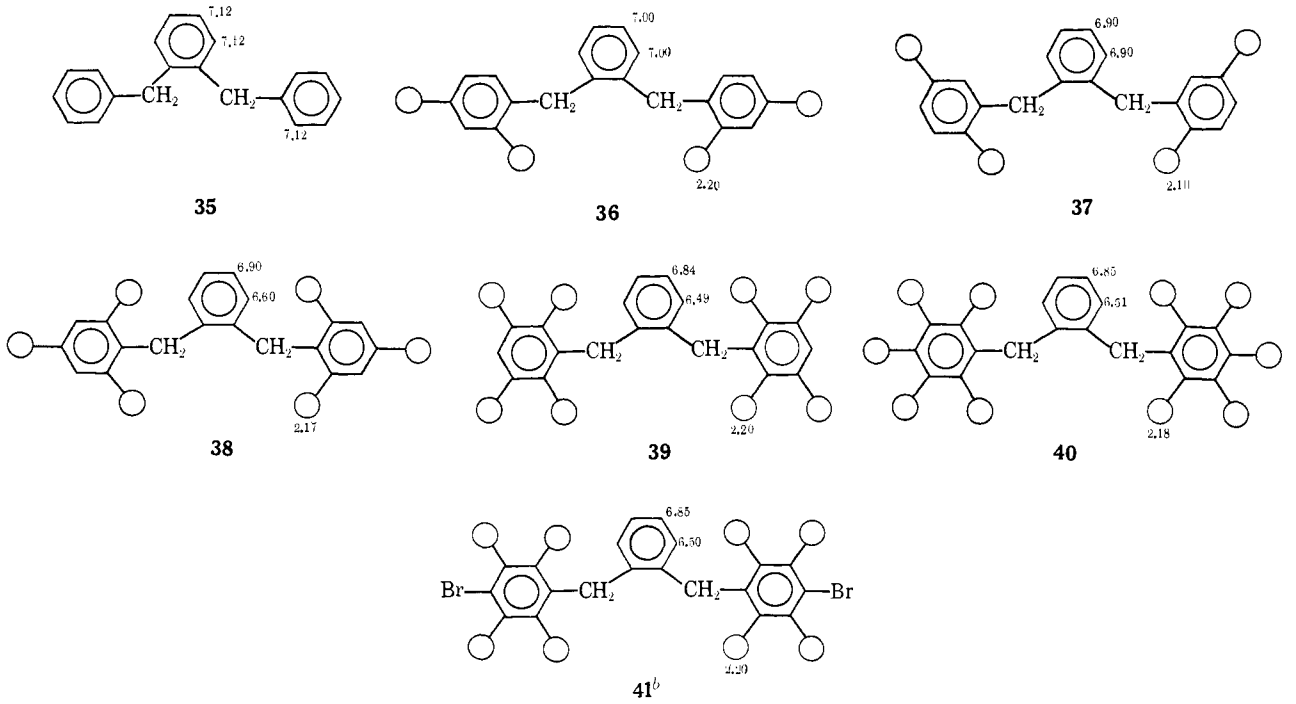
The preponderance of conformer XV is supported also by the fact that compound **41** was measured to have a very low dipole moment. A precise figure was not obtained in this case because of the low solubility in *p*-xylene. However, the estimated value is less than 0.5 D, in good agreement with the value of about 0 D predicted for conformer XV.

Table III. Chemical Shifts[a] of Relevant Groups (O = CH_3) in *m*-Dibenzylbenzenes



[a] Chemical shifts measured in $CDCl_3$ at 30°, in parts per million downfield from TMS as internal standard (60 MHz).

Table IV. Chemical Shifts[a] of Relevant Groups (O = CH_3) in *o*-Dibenzylbenzenes



[a] Chemical shifts measured in $CDCl_3$ at 30°, in parts per million downfield from TMS as internal standard (60 MHz). [b] Measured at 60°.

Table V. Dielectric Constant Data[a]

Compd	w_2	ϵ_{12}	Δn, D
3	0.00000	2.2605	0.000000
a_ϵ = 1.7968	0.00278	2.2659	0.000250
a_n = 0.2694	0.00390	2.2671	0.000366
	0.00459	2.2693	0.000367
	0.00547	2.2698	0.000508
	0.00619	2.2717	0.000561
	0.00720	2.2737	0.000651
7	0.00000	2.2605	0.000000
a_ϵ = 1.4610	0.00272	2.2656	0.000220
a_n = 0.2452	0.00368	2.2662	0.000361
	0.00449	2.2671	0.000377
	0.00569	2.2688	0.000475
	0.00668	2.2713	0.000560
	0.00757	2.2714	0.000658
10	0.00000	2.2605	0.000000
a_ϵ = 0.9483	0.00518	2.2663	0.000442
a_n = 0.2592	0.00621	2.2664	0.000549
	0.00756	2.2682	0.000657
	0.00866	2.2690	0.000762
	0.00964	2.2695	0.000827
11	0.00000	2.2605	0.000000
a_ϵ = 1.0682	0.00270	2.2635	0.000251
a_n = 0.2769	0.00365	2.2640	0.000350
	0.00464	2.2652	0.000492
	0.00554	2.2658	0.000577
	0.00629	2.2673	0.000584
	0.00733	2.2679	0.000661
	0.00817	2.2696	0.000777
13	0.00000	2.2605	0.000000
a_ϵ = 1.2432	0.00224	2.2640	0.000201
a_n = 0.2703	0.00259	2.2638	0.000263
	0.00305	2.2646	0.000276
	0.00394	2.2653	0.000353
	0.00594	2.2681	0.000537
	0.00629	2.2685	0.000601
14	0.00000	2.2605	0.000000
a_ϵ = 1.5034	0.00105	2.2617	0.000106
a_n = 0.2887	0.00320	2.2649	0.000312
	0.00341	2.2655	0.000327
	0.00401	2.2666	0.000396
	0.00410	2.2662	0.000403
	0.00570	2.2690	0.000549
18	0.00000	2.2605	0.000000
a_ϵ = 0.8289	0.00244	2.2624	0.000271
a_n = 0.2660	0.00257	2.2621	0.000251
	0.00334	2.2628	0.000324
	0.00492	2.2643	0.000428
	0.00566	2.2650	0.000559
	0.00705	2.2663	0.000630
21[b]	0.00000	2.2085	0.0000
a_ϵ = 0.4745	0.00201	2.2097	0.0002
a_n = 0.2926	0.00402	2.2104	0.0004
	0.00457	2.2105	0.0005
	0.00484	2.2111	0.0005
	0.00599	2.2111	0.0006
	0.00608	2.2116	0.0006
	0.00680	2.2118	0.0007
	0.00821	2.2126	0.0008
24	0.00000	2.2605	0.000000
a_ϵ = 0.7631	0.00197	2.2621	0.000170
a_n = 0.2743	0.00321	2.2626	0.000265
	0.00338	2.2628	0.000322
	0.00397	2.2638	0.000338
	0.00463	2.2641	0.000435

[a] $a_\epsilon = [(\epsilon_{12} - \epsilon_1)/w_2]_{w_2 \to 0}$, $a_n = [(n_{12}^2 - n_1^2)/w_2]_{w_2 \to 0}$; ϵ_1, dielectric constant of solvent; ϵ_{12}, dielectric constant of solution; w_2, weight fraction of solute; n_1, refractive index of solvent; n_{12}, refractive index of solution. [b] Measurements at 60°; refractive index differences from measurements of refractive index taken with an Abbe refractometer; n_1 = 1.4746; dielectric constant ϵ_1 taken to be 2.2085.

Experimental Section

The syntheses, structure proof, and nmr peak assignments for the compounds discussed in this paper are reported elsewhere.[7]

Dipole moments in Table II have been calculated on the same assumptions used in the case of diphenylmethanes.[2] The dielectric constants (Table V) were measured in *p*-xylene solution at 25 ± 0.01° (for compound **41** at 60 ± 0.02°). Purification of solvent, apparatus used for the measurements of dielectric constants, refractive index differences, and the Guggenheim procedure for the calculation of μ have been described in the preceding paper.[2]

Nuclear Magnetic Resonance. Spectra were obtained using Varian A-60 and Jeol C-60HL high-resolution spectrometers, both working at 60 MHz.

Acknowledgment. We are indebted to the Jeol Co. for running some ^{1}H nmr spectra.

(7) G. Montaudo, P. Finocchiaro, S. Caccamese, and F. Bottino, *J. Chem. Eng. Data*, **16**, 249 (1971).