Conformational Preferences of Bridged Aromatic Compounds. I. Ortho-Substituted Diphenylmethanes[1]

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Abstract: Dipole moments and nmr data are reported for a series of ortho-substituted diphenylmethanes. The results obtained indicate that, depending on the substitution pattern in the four ortho positions, different conformational preferences can arise. The preferred conformations are discussed for each case and good agreement is found between dipole moments and nmr data.

We have been interested in the study of conformational properties of ortho-substituted diphenylmethanes[1] and dibenzylbenzenes[1,2] as a way of exploring the conformational behavior of bridged aromatic compounds[3] and of providing useful models for macromolecular systems.[4]

In our approach, we have coupled dipole moment and nmr measurements to study the conformational preferences eventually induced by ortho substituents in the above mentioned compounds.

Dipole moments, being conformation dependent, are very useful in the study of this kind of molecule, but sometimes do not provide unequivocal information. In fact, due to the angular geometry of these molecules, it may occur that two or more different conformations are calculated to have the same dipole moment value.

We have found[1] that nmr spectra also may provide useful data regarding the conformations of the above compounds. In fact, due to the proximity of the two aromatic rings, the shielding of the ring current[5] of the adjacent nucleus at the ortho position is a function of the molecular conformation. This effect has been systematically investigated by us and the results have been found complementary with those obtained by dipole moments.

In this paper we discuss some data concerning variously substituted diphenylmethanes. The results obtained indicate that, depending on the substitution pattern in the four ortho positions, different conformational preferences can arise.

Stereochemistry of Diphenylmethanes

Diphenylmethane is not a planar molecule in the solid state, its phenyl rings being rotated about 52° out of the plane containing the two C_{Ar}–C bonds.[6,7] This

spatial arrangement also seems preferred by other bridged aromatic systems.[8,9]

On the other hand, it is generally agreed that diphenylmethane does not have a fixed conformation in solution at room temperature.[10–13] Four possible forms involved in its conformational equilibrium are shown in Figure 1. In form A, the two rings are coplanar with each other and with the C_{Ar}–C–C_{Ar} plane. In form B, the rings are perpendicular to the C_{Ar}–C–C_{Ar} plane. In form C, one ring is coplanar and the other perpendicular to the C_{Ar}–C–C_{Ar} plane. Form D stands for the intermediate (skew) conformation.

Although all these forms may be conveniently generated by internal rotation of the phenyl rings around the two C_{Ar}–C axes, structures A and B seem energetically disfavored because of repulsive interactions between nonbonded atoms.[9,10,14] Ortho substitution certainly enhances the energy barrier to internal rotation, and the question arises as to whether it causes this rotation to become restricted, or whether it induces a given conformation to become preferred on steric grounds.[15]

Internal rotation is kinetically restricted in the cyclic compound **1**.[17] Inspection of molecular models indicates that the cycle is unstrained, but the internal rotation of the duryl rings can occur only through an energetically disfavored pathway involving close contacts of the bulky methyl substituents. In open-chain com-

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

(2) See G. Montaudo, P. Finocchiaro, S. Caccamese, and F. Bottino, *J. Amer. Chem. Soc.*, **93**, 4208 (1971).

(3) For work on the present lines on diphenyl ethers and diphenyl thioethers see *Tetrahedron*, **27**, 2125 (1971).

(4) G. Montaudo, F. Bottino, S. Caccamese, P. Finocchiaro, and G. Bruno, *J. Polym. Sci., Part A-1*, **8**, 2453 (1970).

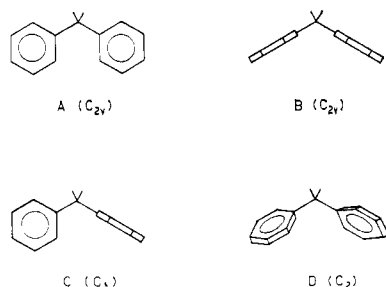(5) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(6) E. J. W. Whittaker, *Acta Crystallogr.*, **6**, 714 (1953).

(7) M. J. Housty, *ibid.*, **14**, 92 (1961).

(8) S. C. Abrahams, *Quart. Rev., Chem. Soc.*, 407 (1956).

(9) J. Boon and E. P. Magre, *Makromol. Chem.*, **126**, 130 (1969).

(10) F. K. Fong, *J. Chem. Phys.*, **40**, 132 (1964).

(11) I. A. Bogdanov and M. F. Vuks, *Vestn. Leningrad. Univ., Fiz. Khim.*, **20** (16) 46 (1965); *Chem. Abstr.*, **64**, 2762e (1966).

(12) M. J. Aroney, R. J. W. Le Fevre, G. L. D. Ritchie, and A. N. Sing, *J. Chem. Soc.*, 5810 (1965).

(13) A. Unanue and P. Bothorel, *Bull. Soc. Chim. Fr.*, 2827 (1965).

(14) K. Higasi and S. Uyeo, *Bull. Chem. Soc. Jap.*, **14**, 87 (1939).

(15) Using nomenclature introduced by Mislow and coworkers,[16] the former process may be called a "kinetically restricted rotation," and the latter a "thermodynamically restricted rotation." This notation will be used in the following.

(16) Y. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, **89**, 4910 (1967).

(17) P. A. Temussi, A. Segrè, and F. Bottino, *Chem. Commun.*, 1645 (1968).

Figure 1. Possible conformations of diphenylmethane. The point group symmetry is indicated in parentheses.

Figure 2. The ortho-substituted diphenylmethanes.

pounds there are alternative pathways, which allow the intramolecular rotation to occur avoiding the energetically disfavored structure A. For diphenyl ethers, a related system, it has been proposed that intramolecular rotation can occur with minimal potential energy barrier if the two twist angles vary in such a way that φ_2 is kept equal to $180° - (90° + \varphi_1)$.[10,18]

1
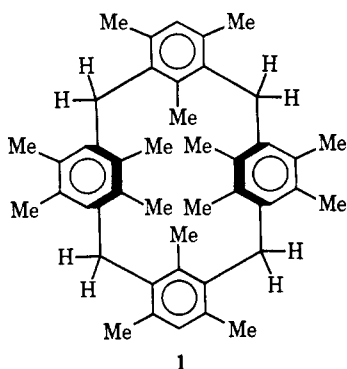
Actually, all the experimental evidence available suggests kinetically unrestricted rotation in diphenylmethane derivatives.[19] Neglecting the nature of the substituent, there are five types of ortho-substituted diphenylmethanes (Figure 2).

Based on steric considerations, there should be little doubt about the forms C and D being preferred in the case of ortho-substituted compounds. In fact, forms A and B, energetically disfavored already in the parent compound, cannot accommodate ortho substituents without undergoing severe deformations. In Figure 3 are shown, as they can be predicted on steric grounds, the preferred conformers for the five types of ortho-substituted diphenylmethanes considered (except for IX, all other forms exist in two enantiomeric structures). Of course, the question arises as to whether these forms actually become preferred, and the answer must be left to the experiments.

Results and Discussion

In Table I are shown the nmr chemical shifts of ortho methyl groups and ortho aromatic protons for a number of diphenylmethane derivatives; chemical shifts of para nuclear hydrogens are also reported for comparison.

The syntheses, structure proof, and nmr peak assignments for these compounds are reported elsewhere.[20]

(18) When considering the internal rotation, both rings must rotate simultaneously around the twist angles φ_1 and φ_2, otherwise the center of gravity of the molecule will be displaced.[10]

(19) Nmr evidence that the rotation does not become kinetically restricted, at least until $-100°$, was obtained by us in the case of diduryl-methane.
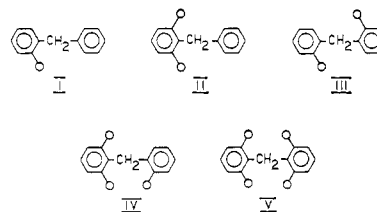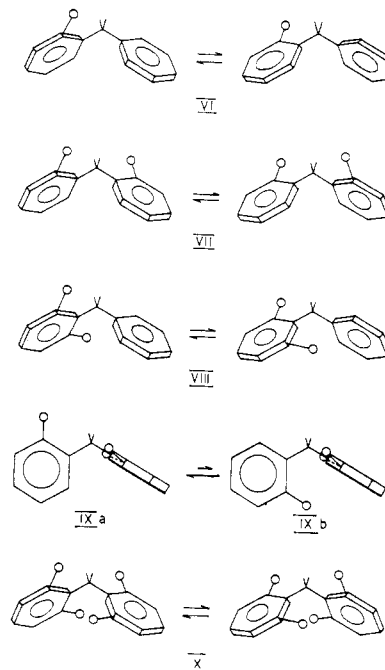

Figure 3. Preferred conformers in ortho-substituted diphenylmethanes.
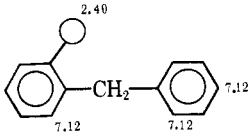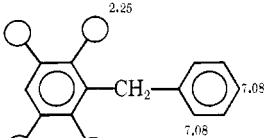
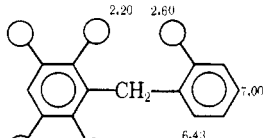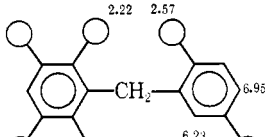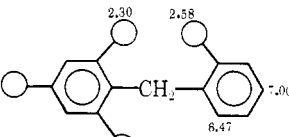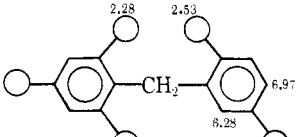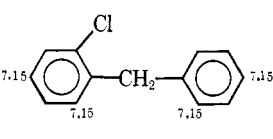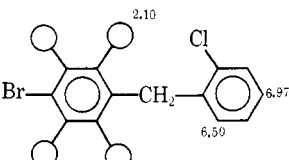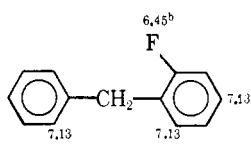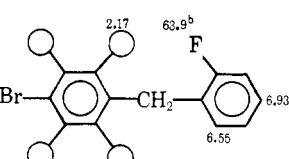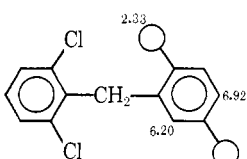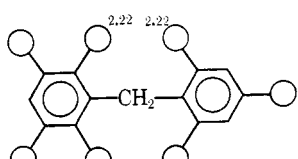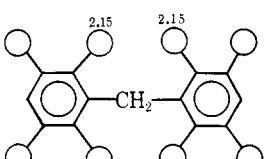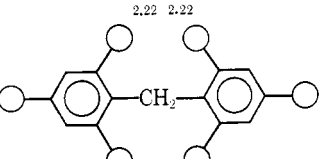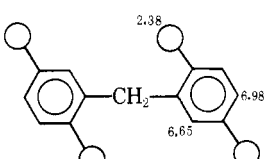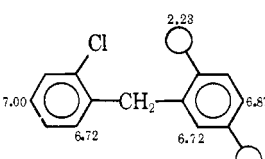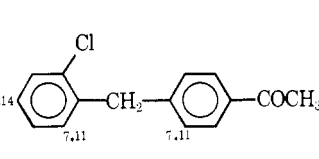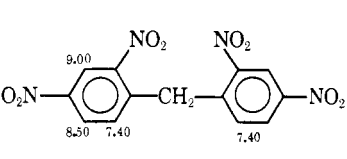The chemical shifts of nuclear protons and methyl groups in the ortho position with respect to the methylene bridge vary markedly depending on the substitution pattern present in the adjacent aromatic ring. Moreover, it is observed that when ortho methyl groups are moved downfield, nuclear ortho hydrogens are moved in the opposite direction. In Figures 4 and 5 are reported some spectra relative to the nuclear aromatic proton region. This effect, as mentioned in the introductory statement, can be accounted for considering the shielding of the ring current[5] of the adjacent nucleus at the ortho substituents.

Data in Table I show that in cases where, from symmetry and steric considerations, a preferred conformation (Figure 3) might be expected to influence the nmr signals of ortho groups, the relative chemical shifts indicate the presence of these forms. On the contrary, in cases where such conformations are not expected to have an effect on nmr signals, the relative chemical shifts appear at average field values.

Going into more detail, when four ortho positions are substituted (13-15, Table I), methyl signals are found at average field values. Averaging must necessarily occur in this case because the coexistence of equivalent conformations with equal population (X, Figure 3) causes each methyl to be exchanged from a shielded position to a deshielded one.

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

Table I. Chemical Shifts[a] of Relevant Groups (O = CH_3) in Ortho-Substituted Diphenylmethanes

Compound **2**: 2.40, 7.12, 7.12, 7.12

Compound **3**: 2.25, 7.08, 7.08

Compound **4**: 2.20, 2.60, 7.00, 6.43

Compound **5**: 2.22, 2.57, 6.95, 6.23

Compound **6**: 2.30, 2.58, 7.00, 6.47

Compound **7**: 2.28, 2.53, 6.97, 6.28

Compound **8**: Cl, 7.15, 7.15, 7.15, 7.15

Compound **9**: Br, 2.10, Cl, 6.97, 6.50

Compound **10**: F, 6.45[b], 7.13, 7.13

Compound **11**: Br, 2.17, 63.9[b] F, 6.93, 6.55

Compound **12**: Cl, Cl, 2.33, 6.92, 6.20

Compound **13**: 2.22, 2.22

Compound **14**: 2.15, 2.15

Compound **15**: 2.22, 2.22

Compound **16**: 2.38, 6.98, 6.65

Compound **17**: Cl, 2.23, 7.00, 6.72, 6.87, 6.72

Compound **18**: Cl, 7.14, 7.11, 7.11, COCH$_3$

Compound **19**[c]: NO$_2$, NO$_2$, O$_2$N—, 9.00, 8.50, 7.40, —NO$_2$, 7.40

[a] Chemical shifts measured in $CDCl_3$ at 30°, in parts per million downfield from TMS as internal standard (60 MHz). [b] Chemical shifts (parts per million) measured in $CDCl_3$ at 30°, 94 MHz, $CFCl_3$ internal standard. [c] 2,4-Dinitrotoluene H_o 7.63 ppm (see Experimental Section).

In compounds where one ring carries two ortho substituents and the other ring is unsubstituted (**3**, Table I), averaging of the methyl and nuclear hydrogen signals must again occur because of the coexistence of equivalent conformations with equal population (VIII, Figure 3).

In the ortho-trisubstituted derivatives (**4-6, 7, 9, 11, 12**, Table I), the two ortho methyl signals belonging to the disubstituted ring appear at average field values. For the monosubstituted ring the ortho methyl signal appears considerably deshielded (0.3-0.4 ppm), the ortho nuclear hydrogen appears shielded (0.5-0.7 ppm), and nmr ^{19}F chemical shifts of compounds **10** and **11** differ by about 0.6 ppm.

These results can be explained only assuming that all these compounds exist predominantly in a form C

where the ortho aromatic hydrogen lies below the adjacent ring. The skew form D becomes sterically disfavored here because of the repulsive interaction between the ortho substituents and the π-electron cloud of the phenyl ring.

Although an equilibrium is formally indicated in IX, Figure 3, it is easily recognized that the steric hindrance forces the mono-ortho-substituted ring in the "inside hydrogen" (IXa) position.

In molecules where there is a single ortho substituent (**2, 8, 10, 18**, Table I), ortho nuclear hydrogens are found at average field values. Chemical-shift averaging must occur for the two ortho protons of the unsubstituted ring because of the rapid interconversion between the two enantiomeric skew forms shown in VI, Figure 3. The ortho nuclear hydrogen belonging to
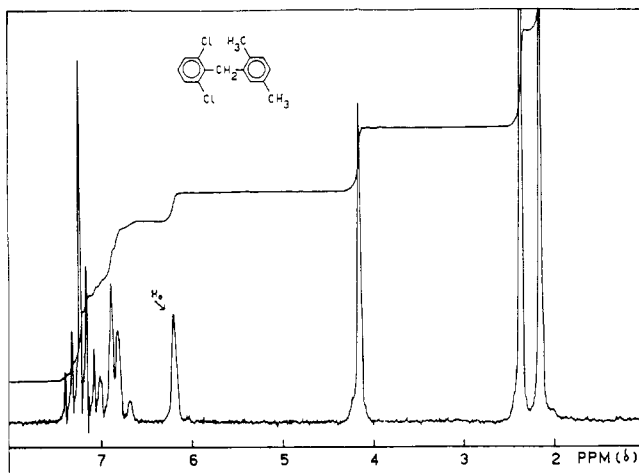
Figure 4. Nmr spectrum of compound 12. The label H_o denotes the peak due to the shielded ortho proton.

Figure 5. Nmr spectra (aromatic region) of compounds 7 and 16. The label H_o denotes peaks due to the shielded ortho protons.

the substituted ring is shielded in both enantiomers, so that no averaging effect can be predicted for it. However, this shielding is probably too little to be detected. Furthermore, due to the absence of other ortho substituents, the aromatic ring can easily oscillate around the equilibrium dihedral angle[21] represented by VI. This situation actually is equivalent to the case where the molecule experiences almost ideal thermodynamically unrestricted rotation,[15] so that the prediction of a preferred conformation VI cannot be tested experimentally.

In compounds where there is one ortho substituent per ring (16, 17, 19, Table I) the ortho hydrogen signals appear shielded upfield, although to a lesser extent with respect to ortho-trisubstituted compounds (about 0.2 ppm). In spite of the fact that in this case also the preferred conformer exists in two skew enantiomeric forms (VII, Figure 3), their interconversion is not expected to cause averaging of the ortho hydrogen signals because these protons are shielded in both enantiomers. As a consequence the observed shielding can be safely attributed to the existence of a preferred conformer, VII. Further support to our conclusions comes from the nmr theory.

It is well known that the ring current induced into the π electrons of a benzene ring by an external magnetic field exerts a shielding or deshielding effect on protons situated in its neighborhood.

The Johnson and Bovey tables[5] provide theoretical shifts for protons in the neighborhood of a benzene ring, and have been widely used to predict the conformation of aromatic compounds.[22]

(21) To speak of torsional oscillations about the equilibrium dihedral angle is the same as to say that the potential energy well is very shallow at its bottom, so that the molecular population becomes distributed over a wide range of torsional angles.

(22) (a) E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **85**, 927 (1963); (b) D. Y. Curtin and S. Dayagi, *Can. J. Chem.*, **42**, 867 (1964); (c) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **86**, 1710 (1964); (d) P. A. Lehman and E. C. Jorgensen, *Tetrahedron*, **21**, 363 (1965); (e) H. A. P. De Jongh and H. Wynberg, *Tetrahedron*, **21**, 515 (1965); (f) T. H. Regan and J. B. Miller, *J. Org. Chem.*, **32**, 592 (1967); (g) H. Kessler, A. Moosmayer, and A. Reiker, *Tetrahedron*, **25**, 287 (1969); (h) E. A. Chandross and C. F. Sheley, *J. Amer. Chem. Soc.*, **90**, 4345 (1968); (i) K. D. Bartle, P. M. G. Bavin, D. W. Jones, and R. L'Amie, *Tetrahedron*, **26**, 911 (1970); (j) C. C. McDonald and W. D. Phillips, *J. Amer. Chem. Soc.*, **89**, 6332 (1967); (k) B. Sheard and E. M. Bradbury, *Progr. Biophys. Mol. Biol.*, **20**, 187 (1970).
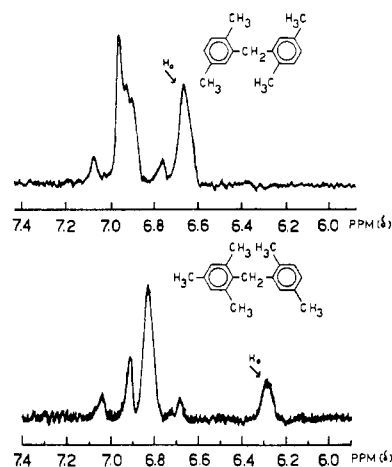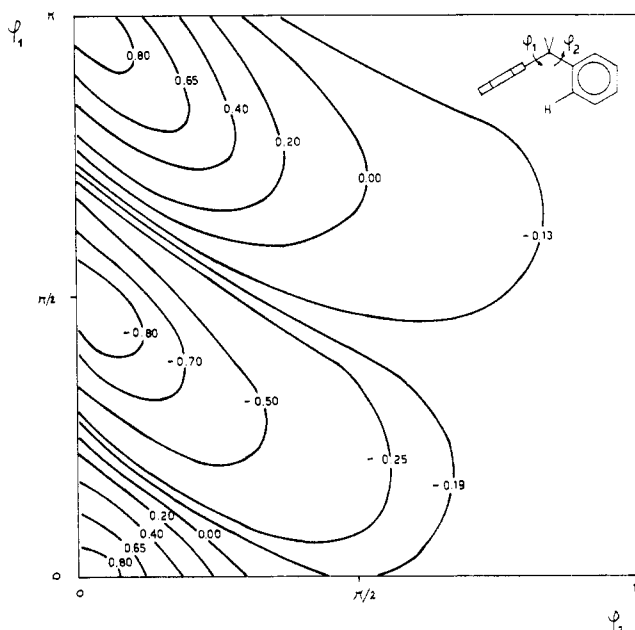
Figure 6. Theoretical shielding values for one of the four ortho aromatic protons of diphenylmethane as a function of the two twist angles φ_1 and φ_2. The figures on the contours represent shielding in parts per million, negative values denoting deshielding. Only the lower left-hand quadrant is shown. The conformation represented in the upper right of the figure is taken as $\varphi_1 = \varphi_2 = 0$.

In diphenylmethane, due to the proximity at the two aromatic rings, the shielding of the ring current[5] of the adjacent nucleus on the ortho positions is a function of the molecular conformation. In order to compare the shieldings predicted by the theory with those found experimentally, we have built[23] a contour map of the theoretical shieldings as a function of the two internal rotation angles, for one ortho aromatic proton in diphenylmethane (Figure 6).

The experimental shieldings (diamagnetic) were computed as the difference between para (H_p) and ortho (H_o) nuclear protons (H_p protons experience a negli-

(23) The map was built assuming the same molecular geometry used to calculate dipole moment values.[6] For each conformation the intramolecular distances were calculated in terms of p and z coordinates by standard trigonometric procedures. The shieldings in parts per million for values of cylindrical coordinates were obtained from the Johnson and Bovey[5] tables.

Table II. Experimental and Calculated Dipole Moments (D) of **9, 11,** and **18** as a Function of the Internal Rotation Angle

	$0°$	$30°$	$60°$	$90°$	$120°$	$150°$	$180°$	Free rotation	Exptl
μ_9	1.43	1.62	2.07	2.55	2.96	3.24	3.32	2.55	1.25
μ_{11}	1.38	1.55	1.95	2.40	2.77	3.00	3.09	2.40	1.29
μ_{18}	2.24	2.46	2.98	3.57	4.09	4.42	4.55	3.57	3.30

The φ header spans the angle columns $0°$ through $180°$.

gible magnetic shielding, about 0.05 ppm, by the neighboring ring current).

For compounds found to exist preferentially in form IXa the experimental chemical-shift difference ranges between 0.5 and 0.7 ppm, while the value inferred from the map in Figure 6 is about 0.8 ppm.

Although the agreement between these figures may be considered acceptable (being of the same order as found in similar cases[22]), it must be said that these molecules may undergo some torsional oscillation around the equilibrium dihedral angle (*i.e.*, the phenyl rings are not fixed). The chemical-shift differences observed may, therefore, represent time-averaged values and this would account for the experimental values being lower than those calculated.[2,24]

For compounds found to exist preferentially in form VII the experimental chemical-shift difference is in the range of 0.2 ppm. The angles of twist inferred from the map in Figure 6 for this shielding correspond to a conformation where the phenyl rings are rotated about 30° out of the plane containing the two C_{Ar}–C bonds. This angle represents, however, a time-averaged value which may not coincide with the equilibrium dihedral angle.

Coming now to discuss the dipole moment data, the inspection of contour maps of calculated dipole moments reveals that, for several substituted diphenylmethanes, it is difficult to assign conformational preferences only on the basis of the experimental values. Experimental data in literature are scarce[12,25,26] and, in general, support the above considerations.

Due to this difficulty, dipole moment measurements were restricted here to cases for which the nmr evidence was strongly in favor of conformational preferences. Halogen atoms were introduced in opportune positions to magnify dipole moment differences among the various possible conformers. Compounds **9, 11,** and **18** were selected as suitable to test the conformational preferences found in ortho-trisubstituted derivatives. Dipole moments of compounds **9** and **11** in the conformation IXa are calculated by us as 1.43 and 1.38 D, respectively, on the following assumptions. (a) The individual moments contributed by each group are 1.56 D as in bromodurene,[26] 1.58 D as in chlorobenzene,[26] 1.35 D as in fluorobenzene[26] and 0.33 D as in diphenylmethane.[26] (b) The valence angle[27] of diphenylmethane, C_{Ar}–C–C_{Ar}, is 120° (from X-ray data available for related molecules[6]). (c) Starting from the

energetically disfavored conformation (A, Figure 1) in which both rings are contained in the C_{Ar}–C–C_{Ar} plane, form IXa is generated rotating the bromodurene ring of 90° with respect to the former plane.

The experimental values, 1.25 **(9)** and 1.29 D **(11)** in *p*-xylene at 25°, come close to those calculated (Table II). The good agreement between values calculated and found is not an accidental one. Considering that the rotation of the bromodurene ring around the C_{Ar}–C axis does not affect the dipole moment value (bromine lies along the C_{Ar}–C axis), the actual dipole moment of the molecule can be calculated as a function of the only remaining internal rotation angle, as reported in Table II.

The dipole moment value is at its minimum for conformer IXa ($\varphi = 0°$, Table II) and steadily increases by varying the angle, up to a limit value of about 3.3 D

Table III. Dielectric Constant Data[a]

Compd	w_2	ϵ_{12}	Δn, D
9	0.00000	2.2605	0.000000
$a_\epsilon = 0.7256$	0.00273	2.2620	0.000231
$a_n = 0.2369$	0.00359	2.2629	0.000289
	0.00371	2.2630	0.000315
	0.00473	2.2638	0.000393
	0.00606	2.2645	0.000525
	0.00693	2.2654	0.000564
	0.00794	2.2662	0.000612
11	0.00000	2.2605	0.000000
$a_\epsilon = 0.7701$	0.00228	2.2619	0.000172
$a_n = 0.2207$	0.00402	2.2635	0.000287
	0.00593	2.2641	0.000421
	0.00702	2.2652	0.000528
	0.00802	2.2667	0.000572
	0.00845	2.2673	0.000643
18	0.00000	2.2605	0.000000
$a_\epsilon = 4.9572$	0.00435	2.2825	0.000318
$a_n = 0.2427$	0.00615	2.2916	0.000458
	0.00731	2.2970	0.000540
	0.00859	2.3037	0.000680
	0.01048	2.3128	0.000840
	0.01223	2.3210	0.000987
19	0.00000	2.2605	0.000000
$a_\epsilon = 5.4948$	0.00261	2.2735	0.000183
$a_n = 0.2472$	0.00475	2.2855	0.000431
	0.00647	2.2942	0.000572
	0.00743	2.3010	0.000625
	0.00948	2.3198	0.000771
4-Acetyldiphenyl-	0.00000	2.2605	0.000000
methane	0.00434	2.2803	0.000349
$a_\epsilon = 4.7773$	0.00572	2.2871	0.000420
$a_n = 0.2345$	0.00739	2.2953	0.000625
	0.00900	2.3034	0.000696
	0.00993	2.3071	0.000776
Bromodurene	0.00000	2.2605	0.000000
$a_\epsilon = 1.2821$	0.00346	2.2648	0.000131
$a_n = 0.1188$	0.00498	2.2669	0.000175
	0.00616	2.2686	0.000264
	0.00699	2.2692	0.000288

(24) The oscillation of the phenyl rings about their equilibrium dihedral angles should be considered each time such a possibility arises in a given molecular structure. In our opinion the confidence in the accuracy of the Johnson and Bovey calculations should increase if this point were properly recognized.

(25) R. S. Tsckhanskii and L. I. Vinogradov, *Zh. Obshch. Khim.*, **32**, 3802 (1962); *Chem. Abstr.*, **58**, 12444*b* (1963).

(26) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

(27) The use of valence angle values of 115 or 110° brings about differences around 0.2 D in the calculated dipole moments.

[a] $a_\epsilon = [(\epsilon_{12} - \epsilon_1)/w_2]_{w_2 \rightarrow 0}$, $a_n = [(n_{12}^2 - n_1^2)/w_2]_{w_2 \rightarrow 0}$; 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.

for the conformer where the ortho halogen atom lies below the adjacent ring ($\varphi = 180°$).

Besides, the average dipole moment value calculated for these molecules with thermodynamically unrestricted rotation and no conformational preference is about 2.5 D.

Molecule **18**, which is not predicted (see above) to be in a preferred conformation, is measured to have a dipole moment value of 3.30 D in good agreement with the value calculated[28] for the thermodynamically unrestricted intramolecular rotation (3.57 D, Table II).

Nmr data (Table I) suggest that a skew form VII is preferred in compounds bearing one ortho substituent per ring. We have measured the dipole moment of compound **19** for which form VII has a calculated moment of about 0 D and thermodynamically unrestricted rotation yields 5.25 D.[29]

The experimental value of 4.25 D comes close enough to that calculated for the latter case. Therefore nmr and dipole moment data seem to be conflicting unless it is assumed that the molecule experiences a large torsional oscillation around the equilibrium (skew) position, as discussed above. This is indeed the explanation we favor at present.

Experimental Section

The syntheses, structure proof, and nmr peak assignments for almost all the compounds discussed in this paper are reported elsewhere.[20]

2,2',4,4'-Tetranitrodiphenylmethane was synthesized according to literature:[30] mp 180–181°; nmr (CDCl₃) δ 9.00 (1), 8.50 (1), 7.40 ppm (1).

2,4-Dinitrotoluene exhibited the following nmr data: (CDCl₃) δ 8.91 (1), 8.38 (1), 7.63 ppm (1).

4-Acetyldiphenylmethane was synthetized according to literature:[31] mp 39°; nmr (CDCl₃) δ 2.40 (3), 3.94 (2), 7.11 (7), 7.75 ppm (2).

2-Chloro-4'-acetyldiphenylmethane. To 11 g (0.055 mol) of 2-chlorodiphenylmethane[20] dissolved in 30 ml of nitroethane was added 7.2 g (0.054 mol) of AlCl₃ dissolved in 30 ml of C₂H₅NO₂. At 0° and with stirring was added dropwise 4.4 g (0.056 mol) of acetyl chloride. After 1 hr the mixture was poured into 5% HCl–water, extracted with CHCl₃, dried (Na₂SO₄), and distilled under vacuum. The white solid obtained (yield 80%) was crystallized from ligroin (bp 60–80°): mp 53–54°; nmr (CDCl₃) δ 2.43 (3), 4.08 (2), 7.11 (6), 7.78 ppm (2).

Anal. Calcd for C₁₅H₁₃ClO: C, 73.62; H, 5.35; Cl, 14.49; mol wt, 244.7. Found: C, 73.78; H, 5.24; Cl, 14.61; mol wt (dichloroethane, 50°), 251.0.

Nuclear Magnetic Resonance. ¹H nmr spectra were obtained using Varian A-60 and Jeol C-60HL high-resolution spectrometers, both working at 60 MHz. ¹⁹F spectra were obtained by a Varian X-100 high-resolution spectrometer equipped with a fluorine probe, working at 94 MHz.

Dipole Moments. The dielectric constants (Table III) were measured in a *p*-xylene solution at 25 ± 0.01° with a DM 01 Dipolmeter WTW. *p*-Xylene (99.9%) (Schuchardt) was dried over molecular sieves. The dielectric constant of *p*-xylene was taken to be 2.2605 at 25°.[32] Attainable measuring sensitivity is about 2 units in the fourth decimal place in the dielectric constant. For refractive indices measurements a differential refractometer BP 2000 V Brice-Phoenix was used which measured the difference in refractive index between a solution and *p*-xylene as solvent, at 25°. Since this apparatus is equipped with a mercury vapor lamp, Δn measured at 436 and 546 mμ were reported at the sodium line values using the Cauchy dispersion formula and refractive indices of *p*-xylene as 1.51366 at 436 mμ, 1.49699 at 546 mμ, and 1.49629 at 589 mμ[32] at 25°.

The differences between Δn values measured at 546 mμ and reported at 589 mμ were very small, sensible only at the fifth decimal place. Use of the above instrument, although time consuming, allows limiting measuring sensitivity of about 3 units in the sixth decimal place of refractive index difference.

For the sake of comparison in Table III dielectric constants and refractive index differences are also reported for *p*-xylene solutions of bromodurene. The dipole moment value found is 1.54 D (lit.[26] 1.56 D).

The dipole moments were calculated as described by Guggenheim.[33]

The final formula (*p*-xylene, 25°) is

$$\mu^2(D^2) = 0.009446 M_2(a_\epsilon - a_n)$$

The probable error of our measurements is ±0.05 D.

(28) The following data are used in this case: valence angle 120°; acetophenone,[26] individual moment 2.96 D; and diphenylmethane,[26] 0.33 D.

(29) The following data are used in this case: valence angle 120°; *m*-dinitrobenzene,[26] individual moment 3.87 D; and diphenylmethane,[26] 0.33 D.

(30) G. D. Parkes and R. H. H. Morley, *J. Chem. Soc.*, 1478 (1936).

(31) M. H. Duval, *Bull. Soc. Chim. Fr.*, 789 (1910).

(32) Landolt-Börnstein, Springer-Verlag, West Berlin, 1967: Vol. II, Part 6, p 621; Vol. II, Part 8, p 635.

(33) E. A. Guggenheim, *Trans. Faraday Soc.*, 47, 573 (1951).