traces of two impurities by TLC ($CHCl_3$–CH_3OH, 9:1, on EtOAc). Precipitation from methanol with water gave a solid, mp 95–99 °C, which was homogeneous by TLC: $[\alpha]^{20}_D$ -14.7° (*c* 1.9, $CHCl_3$).

Anal. Calcd for $C_{32}H_{36}N_3O_8SF_3$: C, 56.54; H, 5.33; N, 6.18. Found: C, 56.38; H, 5.43; N, 6.16.

Tcrom Ester of *tert*-Butoxycarbonyl-L-tyrosylglycylglycyl-L-phenylalaninyl-L-methionine. The tripeptide prepared above (210 mg, 0.30 mmol) was dissolved in dioxane (2 mL) and anisole (0.5 mL) which had been saturated with hydrogen chloride. After 20 min at 25 °C the solvent was evaporated, and the residue was triturated with ether to give the hydrochloride salt of H-Gly-L-Phe-L-Met-OTcrom as a white powder (159 mg, 83%). This was dissolved in 5 mL of freshly distilled DMF containing *tert*-butoxycarbonyl-L-tyrosylglycine (88 mg, 0.26 mmol). The solution was cooled to 0 °C and treated with hydroxybenzotriazole (40 mg), triethylamine (36 μL), and dicyclohexylcarbodiimide (65 mg). After 2 h at 0 °C and 15 h at 25 °C, water and ethyl acetate were added, the slurry was filtered, and the filtrate was evaporated, ultimately at 0.1 mm. The resulting residue was taken up in ethyl acetate, washed with water, 0.5 M citric acid, 5% sodium bicarbonate, and water, and then dried and evaporated. The resulting oil was dried by repeated evaporation of acetonitrile, and the residue was triturated with ethyl acetate to give a white powder (143 mg, 64%) which was homogeneous by TLC ($CHCl_3$–CH_3OH, 9:1): $[\alpha]^{20}_D$ -11.5° (*c* 1.7, CH_3OH–$CHCl_3$, 3:1, v/v).

Anal. Calcd for $C_{43}H_{48}H_5O_{11}SF_3$: C, 57.39; H, 5.37; N, 7.78. Found: C, 57.29; H, 5.50; N, 7.68.

N^α-Boc Methionine Enkephalin. The above Tcrom ester of N^α-Boc methione enkephalin (28 mg, 0.03 mmol) was dissolved in 2 mL of propylamine. After 2 min at 25 °C the amine was evaporated, and the residue was triturated with ether. The bright yellow suspension was filtered, and the collected white solid was dissolved in 5 mL of water. The soluition was filtered, acidified to pH 2–3 with citric acid, and extracted with ethyl acetate, which was then washed with water, dried, and evaporated to yield 20.3 mg (96%) of a white solid, mp 120–135 °C, which was homogeneous by TLC in two solvent systems ($CHCl_3$–CH_3OH–HOAc, 9:1:1, and *n*-butanol–ACOH–H_2O, 7:2:1) and which showed an HPLC trace identical with that of a standard sample (CH_3OH–H_2O, 2:3, flow rate 1 mL/min, μ-Bondapak, C_{18} reverse phase).

Anal. Calcd for $C_{32}H_{43}N_5O_9S$ (for the standard sample): C, 57.04; H, 6.43; N, 10.39; S, 4.75. Found: C, 56.89; H, 6.50; N, 10.36; S, 4.71.

Tcroc-L-alaninylglycine *tert*-Butyl Ester and Tcroc-L-alaninylglycine. A solution of Tcroc-L-Ala-OH (320 mg, 0.90 mmol) and *tert*-butyl glycinate phosphite salt (227 mg, 1.0 mmol) in 3 mL of DMF was cooled to 0 °C and treated with hydroxybenzotriazole (140 mg), triethylamine (130 μL), and dicyclohexylcarbodiimide (220 mg). After 4 h at 0 °C and 12 h at 25 °C, the mixture was worked up as described for the preparation of Boc-Gly-L-Phe-L-Met-OTcrom. The resulting powder was triturated with ether to give 225 mg (53%) of product that was homogeneous by HPLC analysis (CH_3OH–H_2O, 4:1, containing 0.4% HOAc; 1 mL/min, μ-Bondapak C_{18}).

Anal. Calcd for $C_{21}H_{23}N_2O_7F_3$: C, 53.39; H, 4.90; N, 5.93; F, 12.05. Found: C, 53.54; H, 5.04; N, 5.91; F, 11.94.

After 1 h at 25 °C a solution of the above ester (68.5 mg, 0.145 mmol) in 1.5 mL of trifluoroacetic acid was evaporated. Methanol was added (2 × 5 mL) and evaporated to yield a tan solid, 60.6 mg (100%). Recrystallization from acetonitrile gave 54.9 mg (91%), mp 141–143 °C, of Tcroc-L-Ala-Gly-OH.

Anal. Calcd for $C_{17}H_{15}N_2O_7F_3$: C, 49.05; H, 3.63; N, 6.73; F, 13.69. Found: C, 48.83; H, 3.76; N, 6.59; F, 13.58.

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Crystal and Molecular Structure of Diphenylmethane

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The determination of the X-ray structure of diphenylmethane at -70 °C is the first of its kind for a molecule of the type Ph_2ZH_2, where Z is an element of group 4A. Crystals are monoclinic, space group $P2_1/c$, a = 8.875 (11) Å, b = 6.220 (12) Å, c = 20.232 (19) Å, β = 119.89 (9)°. The structure is of the helical type, with ring twist angles of 63.9° and 71.1°. The central C–C–C bond angle of 112.5° is significantly smaller than any such angle previously reported for a ring-substituted diphenylmethane. Empirical force field (EFF) and molecular orbital (EHT, MNDO) calculations indicate a C_{2v} (gable) ground state for the isolated molecule, which is only ca. 0.5 kcal mol^{-1} lower in energy than the helical conformation.

Structural studies of molecules containing at least two substituted or unsubstituted benzene rings attached to a common atomic center are legion: counting X-ray structures alone, 12% of the studies reported in the Cambridge crystallographic database deal with molecules of this description.[2] It is therefore somewhat surprising that not a single X-ray structure has been reported to date for an unsubstituted molecule of the type Ph_2ZH_2 (where Ph = C_6H_5 and Z is an element of group 4A),[4] despite a prodigious amount of work devoted to the conformational analysis of these (and related) compounds. The present study was undertaken in part to remedy this situation.

Diphenylmethane (DPM) was chosen as the target molecule for this investigation since DPM is the parent compound to which all others of the type Ph_2ZH_2, Ph_2ZH, and Ph_2Z may be related as heteroatom derivatives. Also, because DPM is a hydrocarbon, its conformational energies are reliably calculated by the empirical force field (EFF) method.[5] Finally, in contrast to compounds of the types

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(1) (a) The University, Dundee. (b) Princeton University.

(2) This statistic is based on a search covering the literature from 1935[3] and updated to January, 1981. The total number of X-ray structures in this file is 27 551, and the number of hits for the $(C_6^{ar})_2X$ fragment is 3265.

(3) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B* **1979**, *35*, 2331. Wilson, S. R.; Huffman, J. C. *J. Org. Chem.* **1980**, *45*, 560.

(4) To the best of our knowledge, the only X-ray structure reported for a representative of type Ph_2ZH (Z = group 5A element) is that of the 1:1 benzophenone–diphenylamine complex: Brassy, C.; Mornon, J.-P. *Compt. Rend. C* **1972**, *274*, 1728. For type Ph_2Z (Z = group 6A element), there is only one allusion to an X-ray study of diphenyl ether, which is consistent with a helical structure ($\phi_A = \phi_B$ = 17.5°): Katayama, M., unpublished work cited in Higasi, K., *Monogr. Ser. Res. Inst. Appl. Electr., Hokkaido Univ.* **1965**, *13*, 29.

0022-3263/81/1946-4975$01.25/0

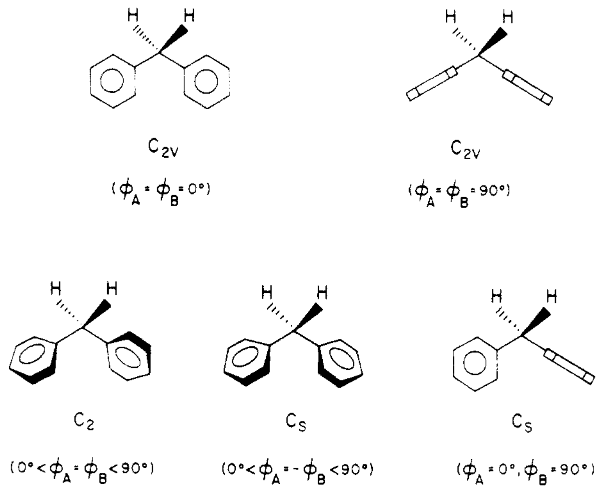

Figure 1. Conformations of diphenylmethane and their point groups; angles of twist in parentheses. Top: planar (left) and gable (right) conformations. Bottom: helical (left) and perpendicular (right) conformations.

Table I. Selected Structural Parameters for Diphenylmethane[a]

atoms	ring A	ring B
	Bond Lengths[b]	
C1-C2	1.412	1.392
C2-C3	1.366	1.397
C3-C4	1.403	1.391
C4-C5	1.387	1.377
C5-C6	1.381	1.389
C6-C1	1.388	1.409
C1-C7	1.501	1.523
	Bond Angles[c]	
C1-C2-C3	122.3	120.6
C2-C3-C4	119.4	119.8
C3-C4-C5	119.5	120.0
C4-C5-C6	120.0	120.8
C5-C6-C1	122.0	119.9
C6-C1-C2	116.8	118.9
C6-C1-C7	121.8	119.1
C2-C1-C7	121.4	122.0
C1A-C7-C1B	112.5	

[a] Bond lengths in angstroms, bond angles in degrees. For numbering scheme, see Figure 2. [b] Estimated standard deviations for bond lengths are 0.009-0.011 Å. [c] Estimated standard deviations for bond angles are 0.6-0.7°.

Ph_2Z and Ph_2ZH, as well as to higher homologues in the Ph_2ZH_2 series, direct conjugative π interaction between the two phenyl rings in DPM is effectively precluded by the insulating methylene group,[6] and the interpretation of conformational behavior is accordingly simplified.

The various conformations of DPM are characterized by the ring twist angles, i.e., the signed dihedral angles ϕ_A and ϕ_B subtended between the least-squares planes of the two rings A and B and the central plane defined by C_A–CH_2–C_B. As shown in Figure 1, the planar and gable[7] conformations have C_{2v} symmetry, and partial desymmetrization of either one by a change in twist angles leads to a family of helical[8] C_2 conformations (which occur as enantiomeric pairs), or to a perpendicular C_s conformation, or to a family of skewed C_s conformations. Complete desymmetrization leads to asymmetric conformations in which $|\phi_A| \neq |\phi_B|$ and in which the twist angles do not assume values of 0° and 90°.

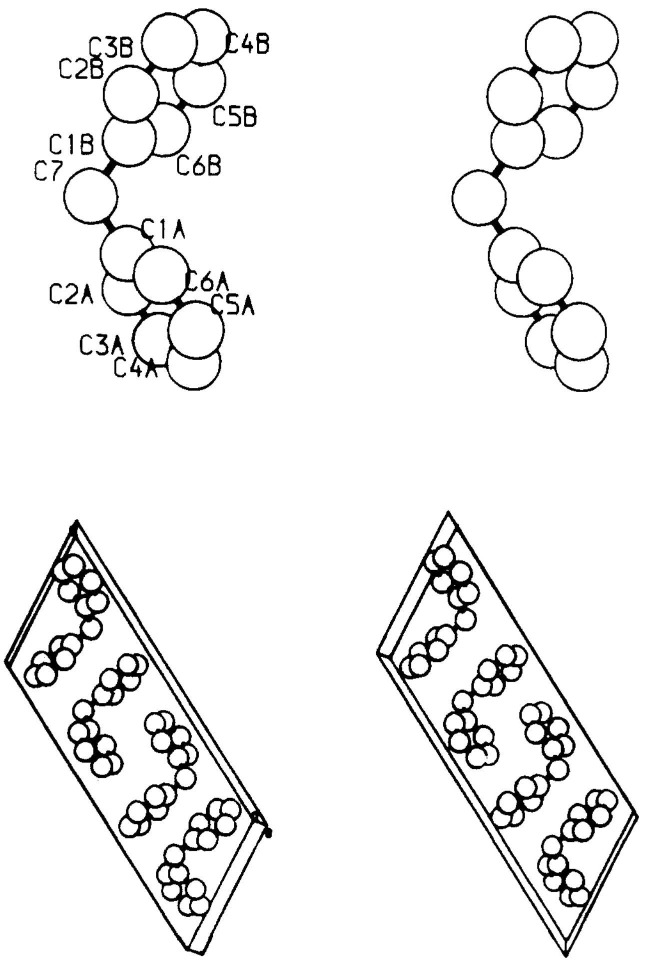

Figure 2. Top: stereoview of the molecular structure of diphenylmethane and numbering scheme for carbon atoms, viewed normal to the C1A–C7–C1B plane. Bottom: packing diagram for diphenylmethane viewed normal to the *ac* plane.

A survey of literature reports dealing with the conformation of DPM in solution reveals that there is no generally agreed upon structure. For example, a helical conformation ($\phi \approx 30$–$42°$) is indicated by Raleigh scattering,[9] Kerr constant,[10,11] and IR intensity[12] measurements. On the other hand, though considered "energetically disfavored" by some,[13] a gable conformation is indicated

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[5] For recent reviews of the EFF method, see: (a) Dunitz, J. D.; Bürgi, H. B. *MTP Int. Rev. Sci: Org. Chem., Ser. One* **1976**, 81. (b) Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161. (c) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (d) Altona, C.; Faber, D. H. *Fortschr. Chem. Forsch.* **1974**, *45*, 1. See also: Mislow, K.; Dougherty, D. A.; Hounshell, W. D. *Bull. Soc. Chim. Belg.* **1978**, *87*, 555.

[6] Lone pairs of electrons on Z in Ph_2ZH and Ph_2Z are in principle capable of conjugative interaction with the phenyl π systems, even though EHT calculations suggest that such interactions may be weak: Galasso, V.; de Alti, G.; Bigotto, A. *Tetrahedron* **1971**, *27*, 6151. In Ph_2SiH_2 and higher homologues, the availability of low-lying *d* orbitals on Z raises the possibility of (p-d)π conjugation, and hence of direct π interaction between the aromatic rings.

[7] Schaefer, T.; Niemczura, W.; Danchura, W.; Wildman, T. A. *Can. J. Chem.* **1979**, *57*, 1881.

[8] Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535.

[9] Rousset, A.; Pacault, A. *Compt. Rend.* **1954**, *238*, 1705. Bothorel, P. *ibid.* **1958**, *246*, 2129. Bothorel, P. *Ann. Chim.* **1959**, *4*, 669. Bothorel, P.; Unanué, A. *Compt. Rend.* **1962**, *255*, 901. Unanué, A.; Bothorel, P. *Bull. Soc. Chim. Fr.* **1965**, 2827.

[10] Aroney, M. J.; Le Fèvre, R. J. W.; Ritchie, G. L. D.; Singh, A. N. *J. Chem. Soc.* **1965**, 5810. Arbuzov, B. A.; Timosheva, A. P.; Vul'fson, S. G.; Vereshchagin, A. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, *29*, 1291.

[11] Helical conformations are also found for 4,4'-dichloro and 4-halo derivatives of DPM by the same method: Calderbank, K. E.; Le Fèvre, R. J. W.; Pierens, R. K. *J. Chem. Soc. B* **1970**, 1115. Chen, S. P.; Huang, H. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1301.

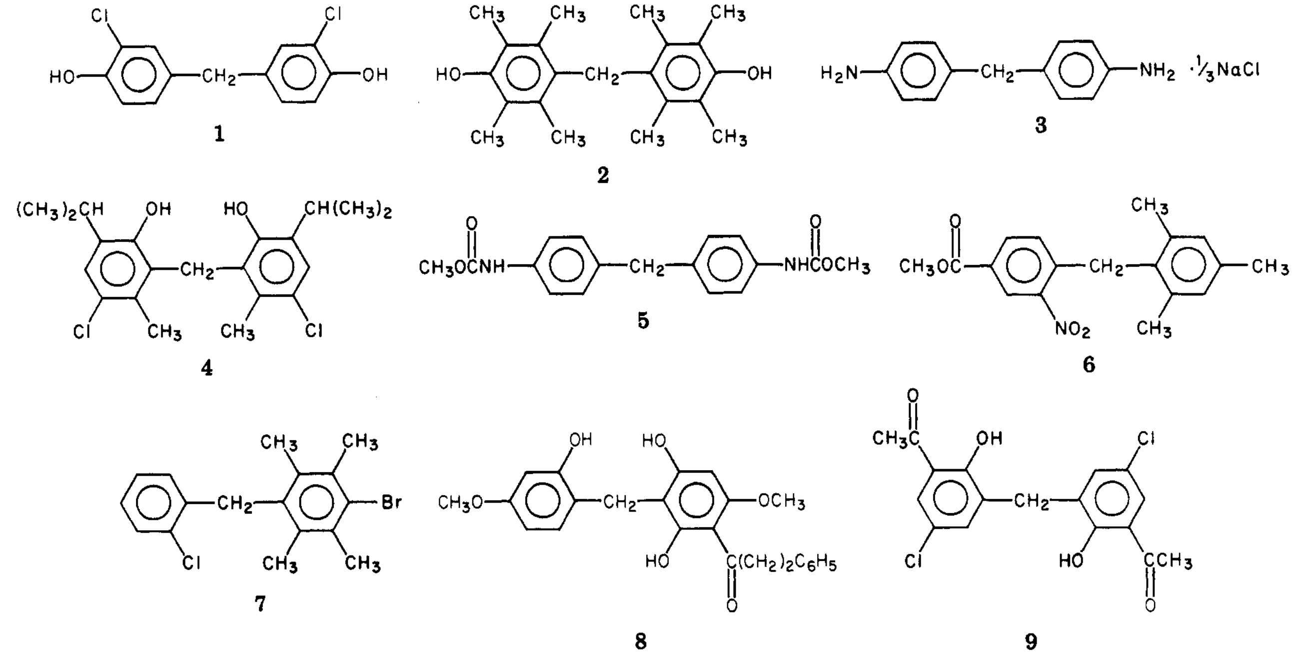
[12] Higuchi, S.; Tsuyama, H.; Tanaka, S.; Kamada, H. *Spectrochim. Acta* **1974**, *30A*, 463. These authors estimate $\phi = 42°$ at room temperature and $\phi = 50°$ in a frozen CS_2 matrix.

Table II. Selected Parameters for X-ray Structures of Ring-Substituted Diphenylmethanes[a]

compd[b]	ϕ_A	ϕ_B	C_A-CH_2-C_B	C_A-CH_2	C_B-CH_2	*R* factor	ref
DPM[c]	63.9	71.1	112.5	1.501	1.523	0.048	*d*
1[e]	52.0	52.0	119.0	1.53	1.53	0.14–0.16	21a
2[e]	43.0	43.0	119.2	1.60	1.60	0.12–0.13	21b
3[f]	49.4	49.4	118.0[g]	1.525	1.525	0.069	21c
4[f]	50.5	66.5	118.6	1.518	1.484	0.056	21d
5[e]	74.5	35.5	114.5	1.514	1.504	0.060	21e
6[f]	2.2	87.6	114.3	1.524	1.513	0.055	21f
7[f]	9.9	86.2	115.9	1.529	1.517	0.088	21g
8[f]	79.5	84.5	116.5	1.518	1.516	0.060	21h
9[f]	81.6	81.3	116.2	1.497	1.520	0.075	21i

[a] Bond lengths in angstrom units, dihedral (ϕ) and bond angles in degrees. [b] Structural formulas for **1-9** are given in the text. [c] Structural parameters for DPM were calculated by the interactive program GEOM and are included for purposes of comparison. [d] Present work. [e] Structural parameters were obtained from the cited literature reference. [f] Structural parameters were calculated by the Cambridge crystallographic database program GEOM78. [g] Reported[21c] 116.7°.

Chart I



by the *J* method[7,14] and Raleigh scattering[15] measurements, as well as by EHT[16] and INDO[7] calculations. Finally, the coexistence of a wide variety of essentially isoenergetic conformations is suggested by Raleigh scattering[17] and ^{1}H NMR[18] measurements and by EFF calculations.[18]

Results and Discussion

The molecular structure of DPM was determined by X-ray analysis.[19] The low melting point of DPM (22 °C) made it inconvenient to collect diffraction data at ambient temperature, and the data were therefore recorded at −70 °C. In agreement with an earlier report,[20] the crystals are monoclinic, space group $P2_1/c$. Stereoviews of the molecule and the packing diagram are shown in Figure 2. Selected bond lengths and angles are reported in Table I and are seen to have typical values. There is no statistically significant difference between any of the ring C–C distances, and the differences in ring angles are only barely significant. Figure 2 clearly shows a helical structure for DPM with approximate C_2 symmetry (ϕ_A = 63.9°, ϕ_B = 71.1°).

It is instructive to compare the structure of DPM with previously reported X-ray structures of ring-substituted derivatives **1–9** (Chart I, Table II).[21]

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(13) Montaudo, G.; Caccamese, S.; Finocchiaro, P. *J. Am. Chem. Soc.* **1971**, *93*, 4202.

(14) Values of $^6J_p^{H,CH}$ and $^6J_p^{F,CH}$ were determined[7] for 3,5-dibromodiphenylmethane and 4,4′-difluorodiphenylmethane, respectively. The conclusion that the gable conformation is the stable form was tentatively extrapolated to DPM. For a recent review of the *J* method, see: Parr, W. J. E.; Schaefer, T. *Acc. Chem. Res.* **1980**, *13*, 400.

(15) Canselier, J.-P.; Clément, C. *J. Chim. Phys.* **1979**, *76*, 699. Of the two solutions found for ϕ, 54.5 ± 1.5° and 81 ± 4°, the latter, which approximates ϕ for the gable conformation, was considered the more probable.

(16) Zubkov, V. A.; Birshtein, T. M.; Milevskaya, I. S. *J. Mol. Struct.* **1975**, *27*, 139.

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

(18) Kornilov, M. Yu.; Zamkovoi, V. I.; Tolstukha, T. A.; Chmilenko, A. N. *Dopov. Akad. Nauk Ukr. RSR, Ser. B: Geol., Khim. Biol. Nauki* **1978**, *4*, 338; *Chem. Abstr.* **1978**, *89*, 599 (*89*, 23654t).

(19) Crystallographic data and final atomic coordinates are listed in the Experimental Section.

(20) Housty, M. J. *Acta Crystallogr.* **1961**, *14*, 92.

(21) (a) Whittaker, E. J. W. *Acta Crystallogr.* **1953**, *6*, 714. (b) Chaudhuri, B.; Hargreaves, A. *ibid.* **1956**, *9*, 793. (c) Swardstrom, J. W.; Duvall, L. A.; Miller, D. P. *Acta Crystallogr., Sect. B* **1972**, *28*, 2510. Jarvis, J. A. J.; Owston, P. G. *Chem. Commun.* **1971**, 1403. (d) Rantsordas, S.; Perrin, M.; Thozet, A. *Acta Crystallogr., Sect. B* **1978** *34*, 1198. (e) Gardner, K. H.; Blackwell, J. *ibid.* **1980**, *36*, 1972. (f) van der Heijden, S. P. N.; Chandler, W. D.; Robertson, B. E. *Can. J. Chem.* **1975**, *53*, 2121. (g) Ganis, P.; Di Blasio, B.; Scippa, C.; Montando, G.; Caccanese, S. *Cryst. Struct. Commun.* **1976**, *5*, 233. (h) Cole, J. R.; Torrance, S. J.; Wiedhopf, R. M. *J. Org. Chem.* **1976**, *41*, 1852. (i) Nowshad, F.; Mazhar-Ul-Haque, *J. Chem. Soc., Perkin Trans. 2* 1976, 623. Not included in this comparison are two molecules containing three $(C_6^{ar})_2CH_2$ fragments: (j) Chetkina, L. A.; Zavodnik, V. E.; Andrianov, V. I.; Sobolev, A. N.; Belsky, V. K.; Tarnopolsky, B. L.; Karpov, L. Ya. *Acta Crystallogr., Sect. A* **1978**, *34*, S110. (k) Hufford, C. D.; Lasswell, W. L., Jr. *J. Org. Chem.* **1979**, *44*, 4709.

Table III. Calculated Conformational Energies for Diphenylmethane

method	conformation[a]	calcd energy[b]	rel energy[c]
EFF	C_{2v} (90.0, 90.0)	3.07	0.00
	C_2 (64.0, 64.0)	3.26	0.19
	C_s (90.0, 0.0)	4.64	1.57
EHT	C_{2v} (90.0, 90.0)	−1130.9459	0.00
	C_2 (64.0, 64.0)	−1130.9120	0.78
	C_s (90.0, 0.0)	−1130.9279	0.42
MNDO	C_{2v} (88.5, 88.1)	−1830.8186	0.00
	C_2 (64.0, 64.0)	−1830.8020	0.38
	C_s (90.0, 0.0)	−1830.7206	2.26

[a] The symmetry of the optimized structure, with the two twist angles (ϕ_A, ϕ_B, degrees) in parentheses. [b] In kcal mol^{-1} for EFF and in eV mol^{-1} for EHT and MNDO. [c] In kcal mol^{-1}.

In **1**, **2**, and **3**, the two halves of the molecule are related by a crystallographic twofold axis which passes through the central carbon atom. Approximate C_2 symmetry is also found in **4**. DPM thus resembles **1**–**4** in that all five molecules are helical, with $\phi \approx$ 50–70°. However, the central bond angle of 112.5° in DPM is substantially smaller than the 118–119° reported for **1**–**4** and somewhat smaller than the 114–116° reported for **5**–**9**. While differences in ring substituents and substitution patterns may in some way be responsible for this effect, it should be noted that the ca. 119° values found for **1** and **2** are expected to be accompanied by rather large standard deviations, given the magnitude of the *R* factors.

The conformations of the remaining structures in Table II cannot properly be described as helical. Intermolecular C=O···HN hydrogen bonds may control the conformation of **5** and are presumably responsible for its asymmetry.[21e] In **6** and **7** the conformation is close to perpendicular, with the ring bearing the ortho-methyl groups (B) perpendicular to the C_A–CH_2–C_B plane, and the lone ortho hydrogen on the A ring proximal to the B ring. Intramolecular steric effects are probably responsible for this "H-inside" conformation, which appears to be the preferred form of triply ortho-substituted diphenylmethanes in solution.[13,22] Finally, **8** and **9** assume approximate gable conformations. While intramolecular OH···O hydrogen bonds partially govern the conformation of the former,[21h] such an explanation is ruled out for the latter, since the phenolic OH groups of the molecule in the crystal bear a trans relationship. The gable conformation found[7,14,15] and calculated[7,16] for DPM is therefore encountered in the X-ray structures of certain ring-substituted derivatives. It should also be noted that from fragmentary information available,[23] it appears that the planes of the aromatic rings in 4,4′-dibromodiphenylmethane are approximately normal to the Br–CH_2–Br plane.

In order to shed further light on this problem, we resorted to EFF and molecular orbital (MO) calculations. With use of the X-ray coordinates for input into the EFF program BIGSTRN-2,[24] unconstrained geometry optimization yielded a C_{2v} gable conformation with C_A–CH_2–C_B = 110.9°. A C_2 structure with ring torsion angles frozen at 64°, but with all other parameters optimized, was calculated to be 0.19 kcal mol^{-1} less stable than the gable conformation, and a C_s structure with torsion angles frozen at 0° and 90° and similarly optimized was found to be 1.57 kcal mol^{-1} less stable (Table III). The C_2 and C_s structures both relaxed to the C_{2v} ground state upon release of the constraint on the torsion angles, followed by geometry optimization. Optimized EFF structures, with C_{2v}, C_2, and C_s symmetries were next used as input into the EHT program EXTHUC,[27] since such hybrid EFF-EHMO calculations have proven useful in the calculation of relative conformational energies.[28] The results (Table III) once again showed the gable conformation to be the ground state, though the relative energies of the other two conformations were reversed. Finally, for calculations by the MNDO[29] method, all but the ortho and methylene protons of the three input structures were frozen at standard values for their bonding parameters, and the phenyl rings were taken to be planar, regular hexagons with C_{ar}–C_{ar} = 1.39 Å. For the C_{2v} input structure, all other parameters were optimized. For the C_2 and C_s input structures, the ring twist angles were frozen as described above, and all other parameters were optimized. The energy differences between the three conformations so calculated (Table III) are very similar to those obtained by the EFF method. For the C_A–CH_2–C_B angle of the C_{2v} structure, MNDO yields a value of 113.4°.

The findings reported in Table III reinforce those of earlier calculations.[7,16,30] However, it is also apparent that the C_{2v} and C_2 conformations are almost isoenergetic: the calculated energy of the former is only of the order of *RT* kcal mol^{-1} below the latter, which in turn is favored entropically by *RT* ln 2 kcal mol^{-1}.[31] The torsional energy minimum must therefore be extremely shallow, and one would expect that the ground-state conformation adopted by DPM would be strongly influenced by its environment. Thus, the helical conformation in the crystal may be imposed by lattice forces. However, such forces must be very weak. The distance between the centroids of the B ring of adjacent molecules across a center of symmetry is ca. 4.4 Å, and there are no very short C···C distances: the closest intermolecular C···C distance is 3.50 Å between C5B and both C5B and C6B of the centrosymmetrically related neighbor. Conformational stability in the solid state is indicated by the absence of phase changes from −100 °C to a few degrees below the melting point. The thermal parameters give no suggestion of any unusual motion—

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(23) Toussaint, J. *Mém. Soc. Sci. Liège* **1962**, *12(3)*, 1. Wilson, A. J. C., Ed. *Struct. Rep.* (*Int. Union Crystallogr.*) **1952**, *16*, 515. The reported Br–CH_2–Br angle is 111 ± 2°.

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(30) Relative energies calculated[7] for DPM conformations by the INDO method are as follows: C_{2v} (gable) 0.0, C_2 1.07, C_s 1.99 kcal mol^{-1}.

(31) This factor is not considered by the computational methods used in this study.

Table IV. Final Atomic Coordinates for Diphenylmethane[a]

atom	x	y	z
C1A	0.4921 (10)	0.3117 (9)	0.1659 (4)
C2A	0.4118 (12)	0.5090 (11)	0.1322 (5)
C3A	0.2375 (10)	0.5423 (11)	0.1020 (4)
C4A	0.1330 (11)	0.3752 (11)	0.1034 (4)
C5A	0.2083 (10)	0.1793 (11)	0.1358 (4)
C6A	0.3852 (11)	0.1506 (11)	0.1670 (4)
C7	0.6843 (9)	0.2799 (11)	0.2001 (4)
C1B	0.7287 (9)	0.1283 (9)	0.1530 (4)
C2B	0.8104 (9)	−0.0685 (9)	0.1815 (4)
C3B	0.8432 (10)	−0.2077 (12)	0.1360 (5)
C4B	0.7979 (11)	−0.1471 (11)	0.0621 (5)
C5B	0.7195 (11)	0.0487 (11)	0.0339 (5)
C6B	0.6846 (11)	0.1877 (10)	0.0783 (4)

[a] Standard deviations in parentheses.

quite the contrary, they suggest that the molecule is rather rigid (see below).

Evidently, the helical structure of DPM in the solid state is at or near an optimum. According to our computational analysis, this observation is not inconsistent with an appreciable population of the gable conformation in solutions of DPM and of derivatives with no ortho substituents, such as **1**, **3**, and **5**. This conclusion is in harmony with the view[16,17,18] that internal motion in DPM is virtually unrestricted, kinetically as well as thermodynamically; in this type of situation a description of the form of the potential hindering rotation may be more meaningful than an enumeration of conformations and their dihedral angles.[32]

Experimental Section

Crystals of diphenylmethane were obtained by sublimation and were mounted in capillaries on a precooled goniometer head which was stored in a refrigerator. The crystals are monoclinic, space group $P2_1/c$, with a = 8.875 (11) Å, b = 6.220 (12) Å, c = 20.232 (19) Å, β = 119.89 (9)°, d_{calcd} = 1.143 g cm^{-3} (−70 °C) for Z = 4 ($C_{13}H_{12}$, M = 168.24). Absorption was negligible, μ(Cu Kα) = 4.1 cm^{-1}. All diffraction patterns were recorded on a Weissenberg camera equipped with a modified Stoe gas-flow cooling device set to maintain −70 ± 2 °C. Close agreement is found between these results and the unit cell parameters reported by Housty from a diffraction study at ambient temperatures.[20] Data were collected from equi-inclination Weissenberg photographs for layers $h(0–5)l$ for a crystal measuring 0.45 × 0.05 × 0.19 mm. A total of 444 reflections had a significant intensity[33] above background.[34] All calculations were performed by using the programs SHELX 76 and XANADU.[35] The structure was solved by using the direct method routine TANG. The best E map showed one phenyl group. Least-squares refinement and Fourier synthesis extended the structure to show all the carbon atoms. Isotropic refinement with hydrogen atoms at calculated positions gave R = 0.082. Individual scale factors were refined for each layer of the Weissenberg data since data about only one axis were available. This limits the validity of refining anisotropic thermal parameters. To minimize the difficulties, U_{22} for each carbon atom was fixed at the average of U_{11} and U_{33}. Single isotropic thermal parameters were refined for the hydrogen atoms. The final discrepancy indices were R = 0.048 and R_w = 0.054 for 127 parameters on the 443 data.[36] Application of Hamilton's test[37] showed that the anisotropic refinement produces an improvement in fit over the isotropic values which is strongly significant at the 0.005 level. The validity of these constrained anisotropic thermal parameters has been examined by the S, L, T librational procedure of Schomaker and Trueblood.[38] Orthogonalized U_{ij} were calculated for each phenyl group separately and for the whole carbon skeleton, assuming a rigid body model in each case. $R_U = \sum|\Delta U_{ij}|/\sum|U_{ij}|$ is 0.072 for each of the phenyl groups and 0.119 for the whole molecule. In each case the ΔU_{22} values are not significantly different from the rest. The results for the phenyl groups show that the observed U_{ij} values are a reasonable representation of the thermal motion. The mean ΔU_{ij} is 0.002 Å^2 compared with a mean σU_{ij} of 0.004 Å^2. As expected the whole molecule is less rigid than a phenyl group but R_U of only 0.119 shows that the librational motions are small. Comparison of the observed U_{ij} values between different atoms shows that the largest libration is a bending motion of C4A···C7···C4B. Final atomic coordinates are listed in Table IV.

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Registry No. Diphenylmethane, 101-81-5.

Supplementary Material Available: Final anisotropic thermal parameters with standard deviations, and observed and calculated structure factors for diphenylmethane (Tables V and VI) (4 pages). Ordering information is given on any current masthead page.

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