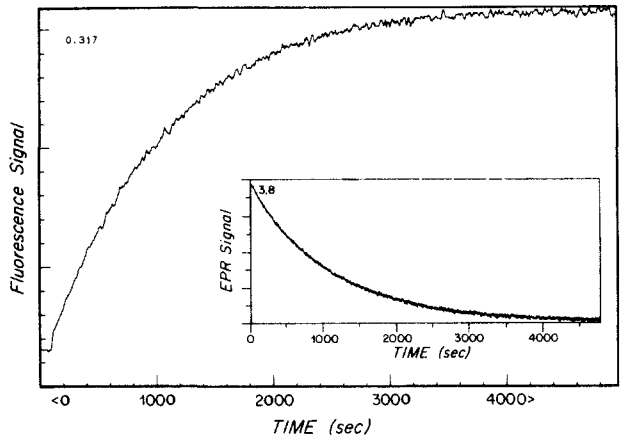

Figure 2. Time courses for the rise of fluorescence and loss of radical spin (inset) following addition of 50 μM ascorbate to a 3 μM solution of **4** in deaerated 50 mM phosphate buffer, pH 8.0; temperature, 24 ± 1 °C. Initially, the base-line fluorescence level of **4** was recorded for ~100 s (λ_{exc}, 330 nm; λ_{em}, 382 nm). Subsequently, a small volume of concentrated, degassed ascorbate solution was injected into the fluorescence cell containing **4**. After mixing, a 50-μL capillary was employed to quickly withdraw a sample for the concurrent measurement of spin loss by EPR. The time course of nitroxide loss was followed at a field position corresponding to the maximum of the low-field nitrogen hyperfine line. Other instrument settings were as follows: microwave frequency, 9.79 GHz; power, 10 mW; modulation frequency, 100 kHz; modulation amplitude, 1.6 G; gain, 3.2×10^6; time constant, 2.5 s. Approximate delay times between sample mixing and initial signal observation were 60 and 250 s for fluorescence and EPR detection, respectively.

paramagnetism and increased yield of fluorescence (Figure 2).[13] The second-order rate constant calculated from these time courses, 19 M^{-1} s^{-1}, agrees reasonably with earlier studies[12] of ascorbate reduction of piperidine nitroxyls.

(13) A quantitative measurement was not feasible for **1** because the ascorbate absorption band significantly attenuated the light at the available excitation wavelengths.

These results show clearly that the fluorescence yield of a compound closely linked to a paramagnetic center can be substantially increased by reactions that lead to a loss of paramagnetism in the center. On this basis, compounds of this class represent a potentially more sensitive and versatile alternative to current methods for radical/redox detection in biological[3,14] and chemical[4] systems. For example, these types of compounds offer the possibility of examining localized radical/redox processes in large, organized assemblies such as cells[14] by fluorescence imaging.

One potential limitation of this approach is that highly reactive radicals such as OH may also react in part with the fluorophore, resulting in its alteration or destruction. We are currently examining this possibility, as well as extending this work to investigate the influence of solvent polarity and viscosity on the fluorescence yields and lifetimes[15] of **1-8**.

Acknowledgment. This work has been supported by the Office of Naval Research under ONR Contract N00014-87-K-0007 NR083-004 and Grant N00014-86-G-0164 issued under the Department of Defense University Research Instrumentation Program for the purchase of the EPR spectrometer. D.J.S. is a recipient of a Surdna Biomedical Postdoctoral Fellowship. We thank Dr. Nelson Frew and Carl G. Johnson for their assistance in obtaining the mass spectra. Helpful comments by Drs. D. Repeta, O. C. Zafiriou, and D. Mauzerall are acknowledged. This is Contribution No. 6532 from the Woods Hole Oceanographic Institution.

Supplementary Material Available: Compound syntheses and characterizations for **1**, **2**, and **4-7** (3 pages). Ordering information is given on any current masthead page.

(14) (a) Swartz, H. M. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 191-202. (b) Stellmach, J. *Histochemistry* **1984**, *80*, 137-143.

(15) Consistent with a rapid intramolecular quenching process, the fluorescence decay of **1** in ethanol is cleanly first order with a lifetime of 190 ps: Mauzerall, D.; Simpson, D. J.; Blough, N. V., unpublished work.

Structure, Resolution, and Racemization of Decakis(dichloromethyl)biphenyl

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Abstract: Decakis(dichloromethyl)biphenyl (**1**) was obtained by photochlorination of decamethylbiphenyl. Crystals of the 1:1 THF solvate are monoclinic, space group $P2_1/n$, a = 17.296 (5) Å, b = 10.091 (3) Å, c = 21.731 (5) Å, β = 96.79 (2)°, Z = 4. The disposition of the dichloromethyl groups on both rings is all-geared, and the molecule has approximate C_2 symmetry. The ^{1}H NMR solution spectrum of **1** is consistent with a time-averaged C_2 conformation. The molecule assumes a curved shape that is well reproduced by empirical force field calculations. Homo- and heterodirectional relationships between subcycles of the molecular model are discussed. Enantiomers of **1** were separated by HPLC on a column of cellulose tris(3,5-dimethylphenylcarbamate). The biphenyl racemizes with a barrier ($\Delta G^{\ddagger}$) of 23.7 kcal mol^{-1}; the threshold mechanism for the enantiomerization most likely involves internal rotation of the dichloromethyl groups rather than rotation of the pentakis(dichloromethyl)phenyl groups about the central biphenyl bond.

Vicinal isopropyl or dichloromethyl groups (CHR_2, R = CH_3, Cl) attached to planar frames such as ethylene and benzene tend to assume gear-meshed conformations in which a methine hydrogen tooth is tucked into the notch created by the methyls or chlorines of a neighboring CHR_2 group.[2,3] A noteworthy feature

(1) (a) Princeton University. (b) Osaka University.

(2) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* **1985**, *18*, 80 and references therein.

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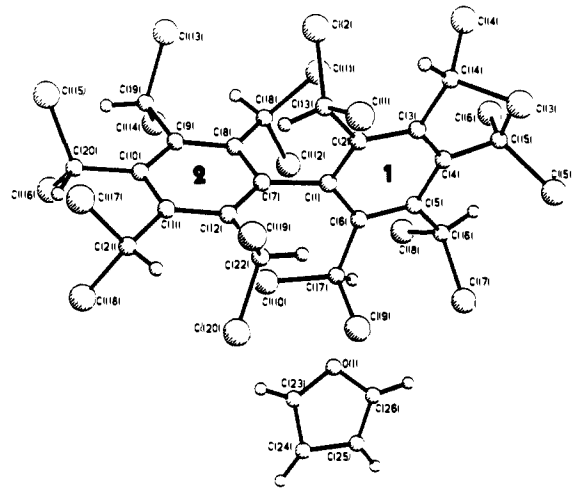
Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **1**·THF[a]



atom	x	y	z	U^b
C(1)	9714 (3)	8347 (6)	3148 (3)	24 (2)
C(2)	9202 (3)	8312 (6)	3595 (3)	23 (2)
C(3)	8522 (3)	7531 (6)	3506 (3)	24 (2)
C(4)	8374 (4)	6745 (6)	2979 (3)	25 (2)
C(5)	8848 (4)	6870 (7)	2500 (3)	29 (2)
C(6)	9491 (4)	7738 (6)	2566 (3)	27 (2)
C(7)	10539 (4)	8882 (7)	3332 (3)	27 (2)
C(8)	11101 (4)	7996 (6)	3614 (3)	26 (2)
C(9)	11843 (4)	8465 (6)	3838 (3)	24 (2)
C(10)	12033 (4)	9811 (7)	3772 (3)	27 (2)
C(11)	11466 (4)	10682 (6)	3490 (3)	25 (2)
C(12)	10723 (4)	10219 (6)	3272 (3)	26 (2)
C(13)	9384 (4)	9210 (7)	4166 (3)	34 (2)
C(14)	7992 (4)	7499 (7)	4017 (3)	32 (2)
C(15)	7735 (4)	5736 (6)	2952 (3)	31 (2)
C(16)	8679 (4)	5983 (7)	1930 (3)	36 (2)
C(17)	9854 (4)	8109 (7)	1973 (3)	40 (2)
C(18)	10989 (4)	6498 (7)	3650 (3)	39 (2)
C(19)	12468 (4)	7592 (7)	4182 (3)	37 (2)
C(20)	12827 (4)	10371 (7)	4004 (3)	39 (2)
C(21)	11630 (4)	12165 (7)	3417 (3)	35 (2)
C(22)	10100 (4)	11119 (7)	2949 (3)	36 (2)
C(23)	10760 (6)	8378 (12)	461 (4)	111 (3)
C(24)	10704 (7)	8555 (13)	−208 (5)	125 (3)
C(25)	10081 (9)	7565 (15)	−419 (5)	166 (3)
C(26)	9809 (8)	7143 (16)	124 (5)	188 (3)
O(1)	10282 (7)	7491 (11)	626 (4)	102 (2)
Cl(1)	8641 (1)	10396 (2)	4227 (1)	42 (1)
Cl(2)	9561 (1)	8323 (2)	4877 (1)	52 (1)
Cl(3)	7025 (1)	7962 (2)	3738 (1)	42 (1)
Cl(4)	8017 (1)	5937 (2)	4400 (1)	49 (1)
Cl(5)	7002 (1)	5909 (2)	2308 (1)	42 (1)
Cl(6)	8108 (1)	4100 (2)	2985 (1)	50 (1)
Cl(7)	8291 (1)	6831 (2)	1245 (1)	52 (1)
Cl(8)	9482 (1)	4996 (2)	1784 (1)	54 (1)
Cl(9)	9315 (1)	9500 (2)	1638 (1)	54 (1)
Cl(10)	10844 (1)	8476 (2)	2037 (1)	56 (1)
Cl(11)	10215 (1)	5908 (2)	4022 (1)	68 (1)
Cl(12)	10957 (1)	5734 (2)	2909 (1)	62 (1)
Cl(13)	12161 (1)	6927 (2)	4871 (1)	57 (1)
Cl(14)	12813 (1)	6333 (2)	3718 (1)	57 (1)
Cl(15)	13025 (1)	10273 (2)	4831 (1)	52 (1)
Cl(16)	13573 (1)	9629 (2)	3632 (1)	55 (1)
Cl(17)	11858 (1)	12981 (2)	4139 (1)	48 (1)
Cl(18)	12364 (1)	12435 (2)	2922 (1)	54 (1)
Cl(19)	9807 (1)	12346 (2)	3455 (1)	50 (1)
Cl(20)	10402 (1)	11903 (2)	2276 (1)	58 (1)

[a] Standard deviations in parentheses. For numbering of atoms, see scheme above, which corresponds to the stereoview in Figure 1. The two rings are identified by boldface numerals. Parameters for hydrogen are given in the supplementary material. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected Experimental and Calculated Structural Parameters for **1**[a]

atoms	exptl (X-ray)	calcd MMP2	calcd MM2(85)
C(1)–C(7)	1.534 (8)	1.534	1.534
C(1)–C(2)–C(13)	117.5 (5)	118.5	118.9
C(1)–C(6)–C(17)	123.0 (6)	121.5	121.6
C(7)–C(8)–C(18)	124.5 (6)	121.0	121.0
C(7)–C(12)–C(22)	117.7 (5)	118.7	118.8
C(2)–C(1)–C(7)–C(8)	84.4 (7)	85.4	90.3
C(2)–C(1)–C(7)–C(12)	−90.5 (7)	−88.8	−87.3
C(6)–C(1)–C(7)–C(8)	−87.5 (7)	−88.2	−93.8
C(6)–C(1)–C(7)–C(12)	97.6 (8)	97.7	88.7
C(7)–C(1)–C(6)–C(17)	−30.1 (9)	−26.0	−18.7
C(2)–C(1)–C(6)–C(5)	−14.1 (9)	−15.2	−19.4
C(6)–C(1)–C(2)–C(3)	8.8 (9)	10.7	15.3
C(8)–C(7)–C(12)–C(11)	0.2 (9)	−2.5	−1.9
C(12)–C(7)–C(8)–C(9)	0.4 (9)	5.9	2.8
C(1)–C(7)–C(8)–C(18)	11.0 (9)	14.2	6.6
C(1)–C(7)–C(12)–C(22)	−6.8 (9)	−8.3	−4.6
C(7)–C(1)–C(2)–C(13)	19.8 (8)	16.7	14.3
C(5)–C(6)–C(17)–Cl(9)	86.5 (6)	81.3	84.6
C(5)–C(6)–C(17)–Cl(10)	−150.2 (5)	−153.2	−150.4
C(4)–C(5)–C(16)–Cl(7)	109.8 (6)	112.4	111.2
C(3)–C(4)–C(15)–Cl(5)	123.0 (5)	118.4	115.4
C(2)–C(3)–C(14)–Cl(3)	124.3 (5)	115.4	117.3
C(1)–C(2)–C(13)–Cl(1)	118.3 (5)	121.5	120.5
C(9)–C(8)–C(18)–Cl(11)	126.3 (5)	126.8	124.1
C(10)–C(9)–C(19)–Cl(13)	117.4 (6)	116.2	114.4
C(11)–C(10)–C(20)–Cl(15)	114.4 (6)	111.3	113.8
C(12)–C(11)–C(21)–Cl(17)	117.3 (5)	114.0	113.9
C(7)–C(12)–C(22)–Cl(19)	116.0 (6)	115.0	115.2
C(4)–M–C(10)[b]	165.2	164.5	166.5

[a] Bond lengths in angstroms, angles in degrees. [b] M denotes the midpoint of the aryl–aryl bond.

of these structures is the conformational cyclic directionality[4,5] imparted by the CHR_2 groups, whose R–C–R angles are bisected by the planar frames. Previous work from our laboratory[3] dealt with the stereochemical consequences of this feature in polysubstituted benzene derivatives. In this paper we extend our analysis to a more complex system, decakis(dichloromethyl)biphenyl (**1**), in which two separate sets of five vicinal dichloromethyl groups are contained in the same molecule, with the sets attached to frames that are essentially perpendicular.

Crystal and Molecular Structure. Exhaustive photochlorination of decamethylbiphenyl afforded **1**, which formed crystals of a 1:1 solvate from tetrahydrofuran. X-ray data for a crystal of the solvate were collected at 193 ± 3 K. The structure was solved and refined by standard least-squares procedures in the space group $P2_1/n$ with 4 molecules in the unit cell. The molecule in the crystal is located on a general position and is therefore asymmetric. A stereoview of **1** is shown in Figure 1, and there appears to be an approximate molecular twofold axis perpendicular to the phenyl–phenyl bond and at an angle of about 45° to the mean plane of each ring. Final atomic parameters are listed in Table I, and selected structural parameters are given in Table II, along with the corresponding values obtained by empirical force field (EFF) calculations (see below).

The 10 dichloromethyl substituents in **1** create a severely crowded environment that induces major deformations in the biphenyl skeleton. Thus, the central phenyl–phenyl bond is substantially elongated, to 1.534 (8) Å as compared with 1.505 (4) Å for bimesityl.[6,7] Even more remarkable is the pronounced

(3) (a) Weissensteiner, W.; Gutiérrez, A.; Radcliffe, M. D.; Siegel, J.; Singh, M. D.; Tuohey, P. J.; Mislow, K. *J. Org. Chem.* **1985**, *50*, 5822. (b) Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569. (c) Singh, M. D.; Siegel, J.; Biali, S. E.; Mislow, K. *Ibid.* **1987**, *109*, 3397. (d) Kahr, B.; Biali, S. E.; Schaefer, W.; Buda, A. B.; Mislow, K. *J. Org. Chem.* **1987**, *52*, 3713 and references therein. (e) Biali, S. E.; Buda, A. B. *Ibid.* **1988**, *53*, 135.

(4) A cycle is defined by three or more non-collinear points in the molecular model. A cycle is undirected if it is bisected by a molecular C_{2n} axis in, or by a molecular σ plane perpendicular to, the mean plane of the cycle. Otherwise it is directed.[3c,5]

(5) Mislow, K. *Chimia* **1986**, *40*, 395.

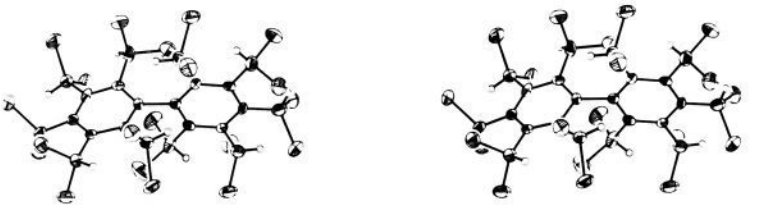


Figure 1. Stereoview of the X-ray structure of decakis(dichloromethyl)biphenyl (**1**) along the approximate C_2 axis, with thermal motion ellipsoids (50% probability).

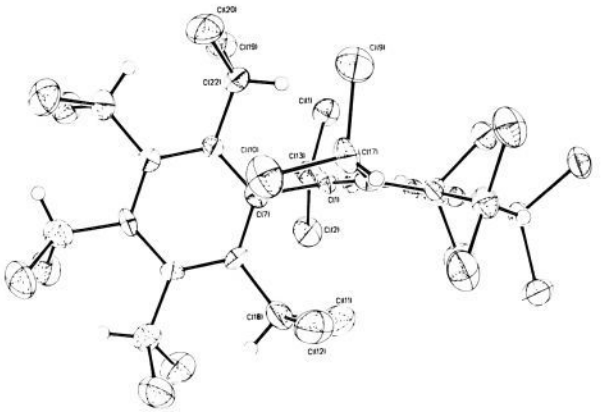


Figure 2. Edge-on view along the normal to the least-squares plane of ring 2 in decakis(dichloromethyl)biphenyl.

cant of the two rings relative to one another, which imparts a curved shape to the molecule (Figure 2): while the least-squares ring planes are perpendicular to one another ($\phi = 89.9°$), as they are in other tetra-ortho-substituted biaryls,[8] the angle defined by the para positions and the midpoint of the central bond (C(4)–M–C(10)) is 165.2°, as compared with 179.2° for the corresponding angle in bimesityl.[6]

Ring 2 is essentially planar: none of the internal C_{ar}–C_{ar}–C_{ar}–C_{ar} torsion angles deviate by more than 2° from zero, and the average absolute deviation of the C_{ar}'s from the least-squares plane, 0.0035 Å, is comparable with the 0.0030- and 0.0027-Å deviations found for the two rings in bimesityl.[6] In contrast, ring 1 assumes considerable twist-boat character: the average absolute deviation of the C_{ar}'s from the least-squares plane is 0.0440 Å, with a 14.1 (9)° torsion for the C(2)–C(1)–C(6)–C(5) angle. Other molecular deformations accompany this distortion in ring 1; for example, the C(6)–C(1)–C(7)–C(12) angle is 97.6 (8)°, as compared with 89.4–91.1° for the analogous angles in bimesityl.[6] Particularly significant is the displacement suffered by the dichloromethyl group attached to C(6) of ring 1. This group has the smallest anti C_{ar}–C_{ar}–C_t–Cl torsion angle [C(5)–C(6)–C(17)–Cl(9) = 86.5 (6)°] and takes on the appearance of a partially slipped gear (Figure 2). As it happens, the same dichloromethyl group is also associated with the THF molecule in the crystal, and the ca. 2.6-Å distance between the furan oxygen and H(17) suggests a weak hydrogen-bonding interaction. Whether this solvent association in the crystal is responsible for the observed torsional effect is a question that we shall address below.

Conformational Analysis and NMR Structure. The presence of two dichloromethyl groups in the para positions of the biphenyl skeleton destroys the C_2 axis that contains these positions. Given that the skeleton is nonplanar, the possible symmetries of **1** are therefore reduced to C_2 (with the C_2 axis bisecting the phenyl–phenyl bond), C_s, and C_1. By analogy with closely related gear-meshed systems,[3] the preferred conformation of the dichloromethyl groups is bisected rather than perpendicular; this leaves C_2 and C_1 as the only symmetries that need to be considered for the ground state of **1**.

If we restrict ourselves to idealized conformations of **1** in which the two rings are planar and mutually perpendicular and in which the dichloromethyl groups are all perfectly bisected, the number of such conformations can be obtained as follows. A given conformation of **1** is represented by a one-dimensional configurational matrix[9] with 10 binary digits, each denoting the orientation of a given dichloromethyl group. Since each such group can assume one of two different orientations, the total number of configurational matrices is 2^{10}. However, a particular structure can be represented by one or more matrices depending on its symmetry,[10] and structures with C_1 and C_2 symmetry are represented by four and two equivalent configurational matrices, respectively. Since there are 2^5 configurational matrices representing the 16 different C_2 conformations, the number of asymmetric (C_1) conformations is $(2^{10} - 2^5)/4 = 248$. The total number of idealized conformations is therefore 264, and since all these structures are chiral, this corresponds to 132 pairs of enantiomers.

The 250-MHz ^{1}H NMR spectrum of **1** in CCl_4 at room temperature is consistent with an all-geared C_2 conformation, in which the two sets of five dichloromethyl groups on the two rings are pairwise homotopic on the NMR time scale. The spectrum consists of five singlets, four in the δ 8.03–8.44 range and the fifth at δ 6.52 (see the Experimental Section).[11] The four downfield signals are assigned to the protons of the four dichloromethyl groups that are tucked into the notch created by a pair of chlorines of a vicinal (ortho) dichloromethyl group and are therefore relatively deshielded. The upfield singlet is assigned to the unique proton that, unlike the other four, experiences the shielding effect of a neighboring benzene ring instead of the deshielding effect of a dichloromethyl gear notch (H(22) and H(13) in Figure 2).

Empirical Force Field Calculations. EFF calculations were performed in order to determine whether the deviations from C_2 symmetry found in the crystal structure are due to packing or solvation effects in the crystal or whether they are intrinsic to the ground-state structure of the molecule in isolation. A further question to be answered was whether the NMR structure corresponds to a single solution conformation of C_2 symmetry or to a time average of two rapidly interconverting C_1 conformations. The programs used were MMP2[12] and MM2(85);[13] the input geometry in both cases was an all-geared, bisected structure of C_2 symmetry ($\phi = 90°$), with standard bond lengths and angles.

Both programs minimized the input geometry to an asymmetric structure that closely resembles the molecular structure of **1** in

(6) Fröhlich, R.; Musso, H. *Chem. Ber.* **1985**, *118*, 4649. Values cited from this paper refer to data collected at 200 K and were in part obtained from supplementary material provided by the Fachinformationszentrum Energie Physik Mathematik.

(7) The central bond length in biphenyl is 1.493 (3) Å. See: Charbonneau, G.-P.; Delugeard, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1586. For a recent summary of structural information on biphenyl, see: Häfelinger, G.; Regelmann, C. *J. Comput. Chem.* **1985**, *6*, 368.

(8) For example, the rings in bimesityl are perpendicular to one another within experimental error.[6]

(9) Willem, R.; Pepermans, H.; Hoogzand, C.; Hallenga, K.; Gielen, M. *J. Am. Chem. Soc.* **1981**, *103*, 2297.

(10) The number of configurational matrices describing a particular isomer is in the inverse order to the symmetry number. See: Brocas, J.; Gielen, M.; Willem, R. *The Permutational Approach to Dynamic Stereochemistry*; McGraw-Hill: New York, 1983; Chapter 8.

(11) A tracing of the spectrum is depicted in Figure 8 of ref 5.

(12) Allinger, N. L. *QCPE* MMP2, **1982**. See: Sprague, J. T.; Tai, J. C.; Yuh, Y.; Allinger, N. L. *J. Comput. Chem.* **1987**, *8*, 581.

(13) Allinger, N. L. *QCPE* MM2(85), **1986**. All calculations were done assuming a nonplanar π system (option NPLANE = 1). The modified torsional parameters for conjugated systems (Liljefors, T.; Tai, J. C.; Li, S.; Allinger, N. L. *J. Comput. Chem.* **1987**, *8*, 1051) were used as implemented in MM2(85).

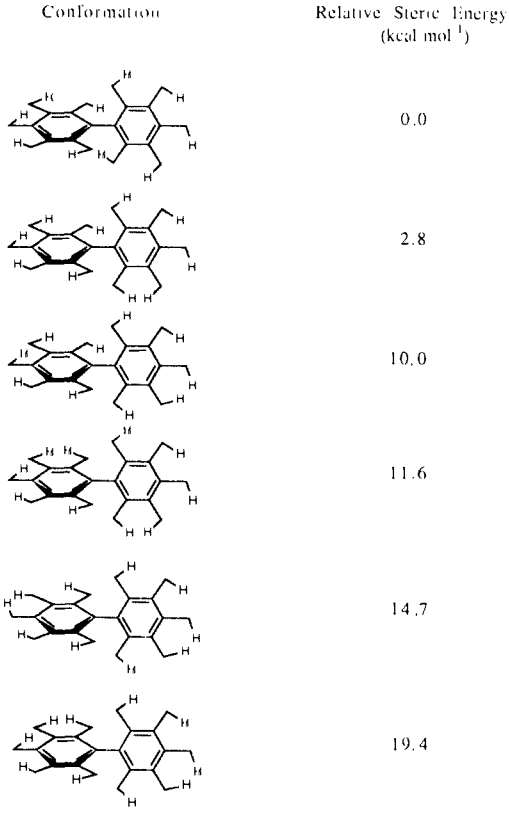


Figure 3. Calculated relative steric energies of selected conformations of decakis(dichloromethyl)biphenyl.

the crystal (Table II). In particular, the elongated phenyl–phenyl bond (C(1)–C(7)), the cant of the two rings (C(4)–M–C(10)), and the gear slippage of the dichloromethyl group attached to C(6) (C(5)–C(6)–C(17)–Cl(9)) are quite well reproduced. In light of the satisfactory correspondence between calculated and observed structures, it is safe to conclude that the molecular structure of **1** in the crystal corresponds to the ground-state structure of the molecule in isolation and that the observed deformations from C_2 symmetry are not the result of crystal-packing forces or solvation effects.[14] Furthermore, the NMR structure is evidently the time average of asymmetric conformations in rapid equilibrium on the NMR time scale.

In previous work on poly(dichloromethyl)benzenes[3d,e] it was found that a gear-clashing interaction in which two pairs of chlorine atoms on vicinal groups are facing each other increases the steric energy by anywhere from 7 to 16 kcal mol^{-1}, whereas in the absence of such interactions the relative steric energy (RSE) does not rise beyond 5 kcal mol^{-1} above the ground state. In all but 6 of the 132 diastereomeric conformations of **1** with bisected dichloromethyl groups there is at least one such interaction. The six conformations and their RSEs (MM2(85)) are depicted in Figure 3, and it is seen that despite the absence of $HCCl_2\cdots Cl_2CH$ interactions between vicinal groups, the RSEs range in value up to 19.4 kcal mol^{-1}. The large steric energies probably result from repulsive inter-ring interactions between the chlorines of the dichloromethyl groups that are facing each other across the phenyl–phenyl bond.[15]

Cyclic Directionality. Let us define a directed cycle[4] for each benzene ring in the idealized all-geared C_2 conformation of **1** by the points corresponding to the C_t's and H's in each set of five dichloromethyl groups. With the spectator point[5] located on the C_2 axis above or below the central bond, the relationship between homotopic (by internal or intramolecular comparison) subcycles within each enantiomer is seen to be homodirectional (Figure 4), whereas the relationship between enantiotopic (by external or intermolecular comparison) subcycles in the two enantiomers is seen as heterodirectional.

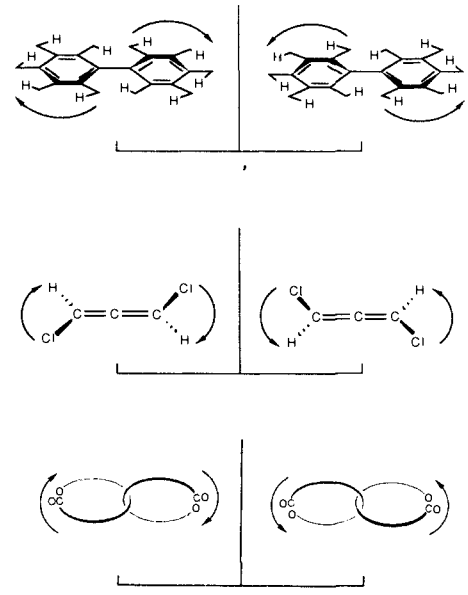


Figure 4. Enantiomeric pairs with C_2 symmetry, viewed along the C_2 axis. The vertical lines symbolize mirror planes at right angles to the plane of the paper. The curved arrows symbolize the sense of cyclic directionality according to an arbitrary convention. Within each enantiomer the relationship between subcycles is homodirectional (by internal comparison), while the relationship between enantiomers is heterodirectional (by external comparison). From the top: (a) The all-geared conformation of **1**; (b) 1,3-dichloroallene; (c) a hypothetical [2]catenane. The circles represent lactone rings of appropriate size.

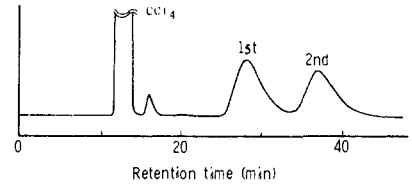


Figure 5. Resolution of decakis(dichloromethyl)biphenyl by chromatography on a cellulose tris(3,5-dimethylphenylcarbamate) column. The eluent is hexane.

The preceding treatment is fully applicable to a host of structural types, such as chiral allenes, biphenyls, and spirans. One of the simplest examples is H_2O_2 in any nonplanar conformation. Since cyclic directionality is defined in terms of molecular symmetry, no consideration need be given to the nature of the bonding arrangements that differentiate biphenyls from allenes, allenes from spirans, and so forth. For example, "topologically chiral" molecules[16] are treated in exactly the same fashion as more conventionally bonded structures (Figure 4).[17]

It remains to be noted that while the two subcycles in conformations of **1** with C_2 symmetry are necessarily homodirectional, this relationship is no longer obvious for asymmetric conformations of **1** since the two subcycles are now symmetry-nonequivalent.[18]

(14) When the symmetry was constrained to C_2, the calculated structure had a relative steric energy of 4.1 (MMP2) or 4.0 (MM2(85)) kcal mol^{-1}. This structure is not a minimum, since removal of the constraint followed by energy minimization led to the ground-state structure.

(15) This effect does not account for the magnitude of all the RSEs, since the interring interaction is similar for conformations with RSEs of 2.8 and 10.0 kcal mol^{-1} (Figure 3).

(16) Walba, D. M. *Tetrahedron* **1985**, *41*, 3161.

(17) It has long been recognized that [2]catenanes made up of two interlocking, constitutionally directed rings are chiral. See: Closson, W., private communication cited by Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789. See also: Sokolov, V. I. *Russ. Chem. Rev. (Engl. Transl.)* **1973**, *42*, 452. Cruse, R. In *Stereochemie der Kohlenstoffverbindungen*; Eliel, E. L., Ed.; Verlag Chemie: Weinheim, 1966; pp 224–225.

(18) The relative sense of directed subcycles in asymmetric molecules must always be arbitrarily defined. Examples are directed cycles constructed from points in the molecular model of simple acyclic molecules, such as CHBrClF or 1-chloro-3-bromoallene, as well as cycles that are identified with constitutionally directed rings, such as the interlocked rings in the asymmetric [2]catenane **11b** described by Schill et al.[19]

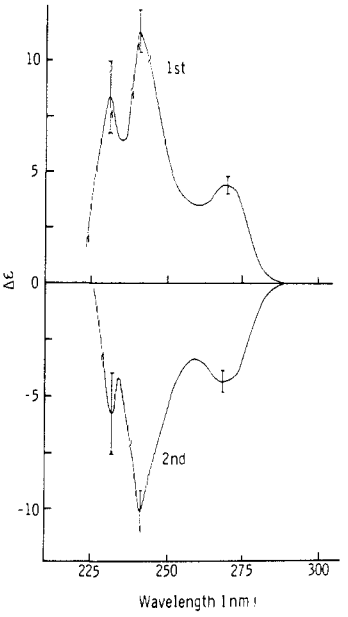


Figure 6. CD spectra of enantiomeric decakis(dichloromethyl)biphenyls in hexane. The first and second fractions (Figure 5) have positive and negative CDs, respectively.

However, the pairwise heterodirectional relationship between enantiotopic subcycles in two asymmetric enantiomers remains unaffected by the absence of an intramolecular symmetry relationship.

Resolution and Racemization. An attempt to resolve **1** by HPLC on a column packed with (+)-poly(triphenylmethyl methacrylate)[20] was unsuccessful, even though this chiral packing material has proven its effectiveness in the resolution of a wide variety of compounds.[21] Separation of the enantiomers was achieved by HPLC on a column of cellulose tris(3,5-dimethylphenylcarbamate),[22] using hexane as eluent (Figure 5). The first and second fraction had an enantiomeric excess (ee) of >99% and 92%, respectively (HPLC). The CD spectra of the enantiomers are displayed in Figure 6.

The resolved compound slowly racemizes at room temperature; the half-life of racemization is 7.8 h at 25 °C. Rates of racemization were measured at 20, 25, and 35°C (see the Experimental Section) and yielded Arrhenius activation parameters E_a = 24.9 kcal mol^{-1} and $A = 4.4 \times 10^{13}$ s^{-1}. From the Eyring equation, $\Delta G^{\ddagger}$ = 23.7 kcal mol^{-1} at these temperatures.

Racemization of all previously known optically active biphenyls occurs by rotation about the phenyl–phenyl bond, through a transition state in which both rings are ideally coplanar. A novel feature of **1** is that racemization can occur either by this conventional process or by rotation of the dichloromethyl side chains. A choice between these mechanistic alternatives becomes possible by comparison of the racemization barrier of **1** with that of (+)-3,3-diaminobimesityl (**2**).[23] The barrier ($\Delta G^{\ddagger}$) estimated[24] for **2** is at least 29.8 kcal mol^{-1}, i.e., the barrier is at least 6 kcal mol^{-1} *higher* than that of **1** even though the four methyl groups in the ortho positions of **2** are substantially *less* bulky than the four dichloromethyl groups in the corresponding positions of **1**. We conclude that **1** enantiomerizes by internal rotation of the dichloromethyl groups rather than by rotation about the phenyl–phenyl bond.[25] This conclusion is strengthened by the observation that the racemization barrier in **1** is comparable in magnitude with the topomerization (homomerization) barrier of 22.2 kcal mol^{-1} in 1,2,3,4,5,6,7,8-octakis(dichloromethyl)anthracene.[27]

A curious feature of this process is that rotation by π of all ten dichloromethyl groups results in homomerization whereas rotation of the five groups on one of the rings results in enantiomerization. That is, even though the two sets of dichloromethyl groups within each enantiomer are seen as homodirectional when viewed from a point on the C_2 axis, it is necessary to restrict reversal of the sense of directionality to only *one* set in order to achieve enantiomerization. The solution to this apparent paradox is that when the five dichloromethyl groups at a given ring are rotated the C_2 axis *reorients in space* and reappears in a orientation perpendicular to the original one.[28] As seen from the reoriented C_2 axis, both sets are necessarily homodirectional. In general, for molecules such as those in Figure 4, reversal of the sense of directionality of one cycle results in enantiomerization, while reversal of the sense of both cycles results in homomerization.

Experimental Section

NMR spectra were recorded on a Bruker WM-250 spectrometer. The high-resolution mass spectrum (static mode peak-matching experiments) was obtained by the Midwest Center for Mass Spectrometry.

Decamethylbiphenyl was prepared in 17% yield by coupling the Grignard reagent of bromopentamethylbenzene[29] in the presence of $CuCl_2$ according to the procedure reported for the preparation of 2,2′,3,3′,4,4′,6,6′-octamethylbiphenyl,[30] mp 237–240 °C (lit.[31] mp 239–241 °C).

Decakis(dichloromethyl)biphenyl (1). A solution of decamethylbiphenyl (170 mg, 0.58 mmol) in 30 mL of CCl_4 was heated under reflux and irradiated with a 150-W lamp while a slow stream of chlorine gas was introduced. After 24 h, the reaction was stopped. The solid that had deposited in the flask and gas inlet was collected (165 mg) and crystallized from 10 mL of carbon tetrachloride to yield 80 mg of product. Recrystallization from 5 mL of tetrahydrofuran afforded 45 mg (7.4%) of crystals of the 1:1 solvate **1**·THF: mp >300 °C; ^{1}H NMR (room temperature, CCl_4) δ 6.52 (s, 1 H), 8.03 (s, 1 H), 8.39 (s, 1 H), 8.40 (s, 1 H), 8.44 (s, 1 H), plus signals due to THF. The stoichiometry of the compound was determined by integration of the ^{1}H NMR signals. High-resolution mass spectrum (only the three most intense signals of the molecular ion cluster are reported), m/z 981.4390 (981.4431 calcd for $C_{22}H_{10}{}^{35}Cl_{16}{}^{37}Cl_4$), m/z 983.4358 (983.4400 calcd for $C_{22}H_{10}{}^{35}Cl_{15}{}^{37}Cl_5$), m/z 985.4353 (985.4370 calcd for $C_{22}H_{10}{}^{35}Cl_{14}{}^{37}Cl_6$).

Resolution and Racemization of 1. A sample of **1** in CCl_4 was placed on a preparative cellulose tris(3,5-dimethylphenylcarbamate) column (50 × 2 cm (i.d.)). Elution with hexane (9.9 mL min^{-1}) yielded well-separated fractions of the two enantiomers, with estimated enantiomeric excess (ee) values of >99% and 92% for the first and second fraction, respectively (Figure 5). The resolving power of the column decreased greatly when hexane/2-propanol (98:2) was used as eluent, and only a single peak was observed. Chromatography on a (+)-poly(triphenylmethyl methacrylate) column (25 × 0.46 cm) also failed to separate the enantiomers.

Solutions of resolved **1** in hexane were held at constant temperature, and samples were withdrawn at fixed time intervals and analyzed by HPLC on cellulose tris(3,5-dimethylphenylcarbamate) at 20 °C. The ratio of enantiomers was estimated from the integrated areas in the chromatograms. At 20 °C the extent of racemization during the chro-

(19) Schill, G.; Doerjer, G.; Logemann, E.; Vetter, W. *Chem. Ber.* **1980**, *113*, 3697. See also comments by Walba,[16] especially p 3172.

(20) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H.; Murata, S.; Noyori, R.; Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971.

(21) Okamoto, Y.; Hatada, K. *J. Liq. Chromatogr.* **1986**, *9*, 369.

(22) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Chromatogr.* **1986**, *363*, 173.

(23) Moyer, W. W.; Adams, R. *J. Am. Chem. Soc.* **1929**, *51*, 630.

(24) A solution of **2** and potassium hydroxide in aqueous ethanol was refluxed for 5 h, resulting in a drop of rotation in **2** from $[\alpha]_D$ 42.3 to 40.7°.[23] From these data a k_{rac} value of 2.14 × 10^{-6} s^{-1} was calculated. We assume that the temperature of the solution (which was not specified) was at least as high as the boiling point of ethanol (78.5 °C).

(25) This process is somewhat reminiscent of the enantiomerization mechanism in (*R*)-menthyl (*S*)-menthyl 2,2′,6,6′-tetranitro-4,4′-diphenate (**3**). All conformations in this compound are chiral and enantiomerize by internal rotation of the carbomenthyloxy side chains rather than by rotation about the phenyl–phenyl bond.[26] However in **3**, which is formally a meso compound, enantiomerization occurs exclusively through chiral pathways, whereas in **1** achiral as well as chiral pathways are conceivable.

(26) Mislow, K. *Science (Washington, D.C.)* **1954**, *120*, 232. Mislow, K.; Bolstad, R. *J. Am. Chem. Soc.* **1955**, *77*, 6712.

(27) Biali, S. E.; Buda, A. B.; Mislow, K. *J. Org. Chem.*, in press.

(28) For a related example of an S_4 axis reorienting in space as a consequence of internal rotations, see: Hutchings, M. G.; Nourse, J. G.; Mislow, K. *Tetrahedron* **1974**, *30*, 1535. Nourse, J. G.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 4571.

(29) Smith, L. I.; Nichols, J. *J. Org. Chem.* **1941**, *6*, 489.

(30) Knauf, A. E.; Adams, R. *J. Am. Chem. Soc.* **1933**, *55*, 4704.

(31) Smith, L. I.; Paden, J. H. *J. Am. Chem. Soc.* 1934, *56*, 2169.

matographic analysis was at most 2–3% and was therefore not taken into account in the analysis of the data. Attempts to carry out the chromatographic analysis at 15 °C were unsuccessful because of extensive broadening of peaks.

Racemization rate constants (k) at 20.2, 25.0, and 35.0 °C are 1.25, 2.48, and 9.67 × 10^{-5} s^{-1}, with correlation coefficients of 0.999. Calculated activation parameters are given in the text.

X-ray Crystallography. Crystals of decakis(dichloromethyl)biphenyl containing 1 mol equiv of THF were obtained from tetrahydrofuran by slow evaporation at room temperature. The crystals of the solvate did not effloresce appreciably on standing in air at room temperature for several months. A crystal of approximately 0.05 × 0.20 × 0.23 mm^3 was chosen for the X-ray measurements. Crystal data: $C_{22}H_{10}Cl_{20}\cdot C_4H_4O$, M_r 1051.0; monoclinic (space group $P2_1/n$ assumed throughout); a = 17.296 (5) Å, b = 10.091 (3) Å, c = 21.731 (5) Å, β = 96.79 (2)°, V = 3766 (2) $Å^3$, d_{calcd} = 1.85 g·cm^{-3}, Z = 4. X-ray intensities were measured at 193 ± 3 K on a Nicolet R3m four-circle diffractometer equipped with a nitrogen-flow cooling device by applying Cu Kα radiation (λ = 1.541 78 Å). A total of 5902 reflections were recorded with $h, k \geq 0$ and with $3° \leq 2\theta \leq 110°$. Of these, 3570 with $[|F_0| > 3\sigma(F_0)]$ were considered unique and observed. Absorption corrections were applied analytically by approximating the crystal shape as a rectangular plate. The structure was solved by direct methods with the SHELXTL software. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at ideal positions (C–H = 0.96 Å and C–C–H = 109.5, 120.0°). The oxygen scattering factor was assigned to each position in the THF ring and refined; in all positions other than that near H(17) the R factor was ca. 0.4% higher. R and R_w after refinement were 0.057 and 0.047, respectively.

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Registry No. 1, 112375-38-9; (+)-**1**, 112375-40-3; (−)-**1**, 112375-39-0; decamethylbiphenyl, 18356-20-2.

Supplementary Material Available: Bond lengths and bond angles, with standard deviations for **1** (Tables III and IV), final anisotropic thermal parameters for non-hydrogen atoms (Table V), and atomic and thermal parameters for hydrogen (Table VI) (4 pages). [The structure factor table is available from the author.] Ordering information is given on any current masthead page.

Photoaddition and Photoreduction of Chloranil with Arenes via Singlet and Triplet Excited Complexes: Effects of Irradiation Wavelength and Radical Ion Pair Spin Multiplicity

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Abstract: The photochemistry of chloranil (Q) in the presence of the arenes hexamethylbenzene, 1-methyl-, 1,3-dimethyl-, 1,4-dimethyl-, and 2,3-dimethylnaphthalene, and acenaphthene has been investigated. Irradiation in a nonpolar solvent provided ether adducts resulting from formal addition of the quinone to the arene side chain, the hydroquinone, (QH_2), and in one case, an identifiable oxidation product, acenaphthylene. The quantum yield for these transformations was shown to have a complex dependence on the concentration of the arene and the irradiation wavelength. On irradiation at 366 nm under conditions in which free chloranil absorbs, the preferred product was the reduced species, QH_2. On irradiation at 436 nm under conditions in which the ground-state charge-transfer (CT) complex of Q and the arene chiefly absorbs, the preferred product was the ether adduct. Excitation of complexes at 546 nm resulted in a sharply reduced quantum yield. Flash photolysis studies show that the quenching of Q triplets by the arenes leads to free radicals ($QH^\bullet$ and $DH^\bullet$) by a sequential electron-transfer, proton-transfer mechanism. Irradiation of Q/DH_2 complexes appears alternatively to lead to singlet radical ion pairs ($Q^{\bullet-}$,$DH_2^{\bullet+}$) which evolve into singlet radical pairs ($QH^\bullet$,$DH^\bullet$) and final products in competition with back reactions which return radical pairs to ground-state reactants. The wavelength dependence of product quantum yield for excitation of Q/DH_2 complexes is discussed in terms of the facilitation of proton transfer within radical ion pairs due to the ability of side-chain C–H bonds of the arenes to act as acceptor modes for deposition of excess vibrational energy in charge transfer excited states.

The photochemistry of the "high-potential" quinone, chloranil (Q), was shown in early studies to involve photoaddition reactions and hydrogen atom abstraction from a variety of substrates (e.g., alcohols and aldehydes).[1] In more recent investigations molecular rearrangements that proceed via radical cation intermediates have been observed as the result of reductive quenching of the Q triplet excited state.[2] Several studies that have employed picosecond or nanosecond time-resolved laser flash techniques have led to the identification of transient species on electron transfer between ^3Q and aromatic hydrocarbons.[3] Although the tendency for quinones to form ground-state complexes with potential reactants is well-known,[4] the importance of excitation of complexes in chloranil photochemistry is not well understood. In the early investigations of chloranil photochemistry,[1] there are intimations of the importance of ground-state quinone complexes in photoaddition reactions (unusual concentration dependences). In a recent phototransient and CIDNP study of indene complexes of Q, only the route involving excitation of uncomplexed Q and triplet quenching was verified for photolysis of Q in the presence of moderate concentrations of the electron donors.[3a]

In a series of investigations of the photochemistry of ground-state, charge-transfer (CT) complexes of varied electron donors and acceptors, a wavelength dependence of product quantum yields has been observed.[2c] This unusual dynamical feature for excited complexes (CT*) shows considerable generality (e.g., electron transfer induced hydrocarbon rearrangements[5] and ionic disso-

(1) For a general review, see: Bruce, J. M. In *The Chemistry of Quinonoid Compounds*; Patai, S., Ed.; Wiley: New York, 1974; Part 1, Chapter 9.
(2) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1984**, *106*, 6053. (b) Roth, H. D.; Schilling, M. L. M. *Ibid.* **1981**, *103*, 1246. (c) Jones, G., II; Becker, W. G. *Chem. Phys. Lett.* **1982**, *85*, 271. (d) Jones, G., II; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805.
(3) (a) Rentzepis, P. M.; Steyert, D. W.; Roth, H. D.; Abelt, C. J. *J. Phys. Chem.* **1985**, *89*, 3955. (b) Kobashi, H.; Funabashi, M.; Kondo, T.; Morita, T.; Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3557. (c) Gschwind, R.; Haselbach, E. *Helv. Chim. Acta* **1979**, *62*, 941.
(4) See: Foster, R. In ref 1, Chapter 7.
(5) (a) Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1269. (b) *Ibid.* **1983**, *105*, 1276.

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