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Molecular Structure of Hexakis(dichloromethyl)benzene

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The crystal and molecular structure of hexakis(dichloromethyl)benzene (2) has been determined. Crystals of 2 are triclinic, space group $P\bar{1}$: $a = 6.248\ (1)$ Å, $b = 9.749\ (3)$ Å, $c = 9.763\ (2)$ Å, $\alpha = 116.32\ (2)°$, $\beta = 94.97\ (2)°$, $\gamma = 108.20\ (2)°$, $Z = 1$. The crystal structure and the dimensions of the unit cell closely resemble those previously found for hexaisopropylbenzene (1), and the molecules of 2, like those of 1, closely approximate C_{6h} symmetry in the crystal. A crystallographic orientational disorder was resolved, and the population ratio of major and minor orientations, 1.827, was found to be similar in magnitude to the corresponding ratio for 1, 2.075. Empirical force-field calculations have revealed that in contrast to 1,2-bis(dichloromethyl)- and pentakis(dichloromethyl)benzene, the conformations of lowest energy in 1,2-diisopropyl- and pentaisopropylbenzene are not gear-meshed and that 1 is unique among vicinally substituted polyisopropylbenzenes in having a ground-state conformation with homodirectional isopropyl groups.

The six vicinal isopropyl groups in hexaisopropylbenzene (1) are tightly gear-meshed and immobilized on the laboratory time scale.[2] Because methyl and chloro groups are comparable in size[3] it became of interest to examine the structure of the dichloromethyl analogue of 1, hexakis(dichloromethyl)benzene.[4] The synthesis of this compound was first reported by Imhof, working in Hopff's laboratory.[5] According to the ETH group,[5,6] the conformational similarity between 1 and 2 is suggested by space-filling models and by the appearance of a sharp band of medium intensity at 3080 and 3085 cm^{-1} in the infrared spectra of 1 and 2, respectively, due to a strongly perturbed methine C–H stretching vibration. The low-field singlet at δ 8.3 in the ^{1}H NMR spectrum of 2[5,7] is also consistent with a gear-meshed conformation in which the proton is located between the chlorines of a neighboring dichloromethyl group and in which van der Waals interactions lead to a downfield shift.

Crystal Structure of Hexakis(dichloromethyl)benzene. This work was undertaken in order to determine whether the conformational similarity between 1 and 2 suggested by the spectroscopic data is manifested in the molecular structure of 2. X-ray data for a crystal of 2 grown from heptane were collected at 175 K. The structure of 2 was solved and refined by standard least-squares procedures in space group $P\bar{1}$, with one molecule per unit cell centered on a special position. As in the case of 1,[2] two unique positions for each symmetry nonequivalent tertiary carbon (C_t) were found, but only single average aromatic carbon (C_{Ar}) and chlorine positions could be obtained. Splitting the populations of the C_t's between two sites per carbon (C_t = major orientation, C_t' = minor orientation) resulted, after refinement, in a ca. 2:1 ratio of electron densities between the sites corresponding to each unique C_t. As shown in Figure 1, the striking similarity in the molecular conformations and in the cell constants of 1 and 2 indicates that the two compounds are isomorphous.

In analogy with 1,[2] the disorder in 2 could be modeled by an arrangement of flipped rings in which enantiotopic faces are exchanged. However, such modeling, based on the weighted average least-squares positions of C_{Ar}(av) and Cl(av) and on the resolved locations of C_t (i.e., on C_t and C_t') resulted in dramatic exocyclic angular distortions even greater in magnitude than those obtained in the analogous treatment of 1.[2] Similarly, the elongation of the anisotropic thermal motion ellipsoids of C_{Ar}(av) tangential to the ring was found to be even greater in 2 than in 1 (Figure 1). From these observations and by analogy with 1,[2] it could be concluded that the distance between the crystal positions of corresponding aromatic carbons in the two orientations ($d(C_{Ar}–C_{Ar}')$) is greater in 2 than in 1, i.e., that the two orientations have similar geometries and that the two flipped rings are rotated with respect to one another

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(2) Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569.

(3) Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* **1980**, *20*, 65 and references therein.

(4) A portion of this work was reported in a preliminary communication: Mislow, K. *Chimia* **1986**, *40*, 395.

(5) Imhof, W., Dissertation ETH, Zürich, 1964 (Prom. No. 3507), pp 22–24, 48–49. See also: Hopff, H. *Chimia* **1964**, *18*, 140.

(6) Hopff, H.; Gati, A. *Helv. Chim. Acta* **1965**, *48*, 509.

(7) Mark, V.; Pattison, V. A. *J. Chem. Soc., Chem. Commun.* **1971**, 553. See also: Hutton, H. M.; Hiebert, W. E.; Mark, V. *Can. J. Chem.* **1978**, *56*, 1261.

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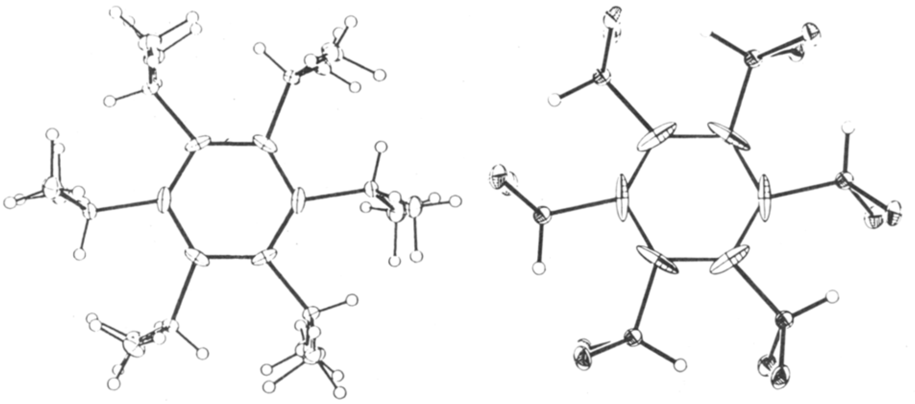

a	6.400(2) Å	6.248(1) Å
b	9.943(3) Å	9.749(3) Å
c	10.223(2) Å	9.763(2) Å
α	117.79(2)°	116.32(2)°
β	94.78(3)°	94.97(2)°
γ	105.58(3)°	108.20(2)°
V	536.7 Å^3	488.4 Å^3

Figure 1. A comparison of unit cell constants for hexaisopropylbenzene (**1**, left) and hexakis(dichloromethyl)benzene (**2**, right). Both molecules crystallize in space group $P\bar{1}$, with one molecule per unit cell. The ORTEP drawings depict the major orientation of the molecules, with thermal motion ellipsoids (50% probability) based on resolved C_t positions and average unresolved C_{Ar} positions.

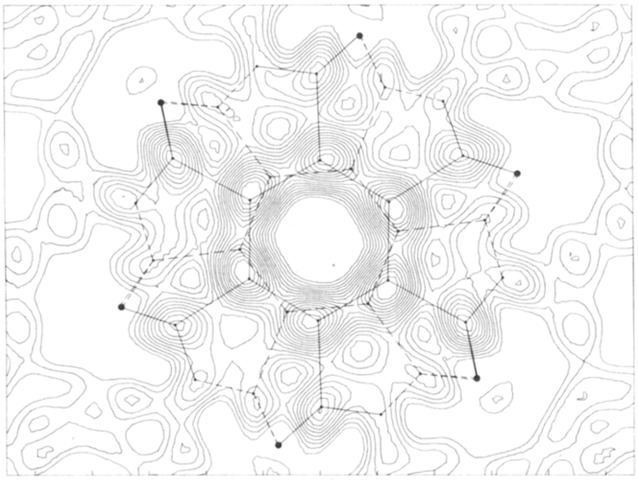

Figure 2. Electron density section of **2** through the least-squares plane of the benzene ring. Contour intervals are at 0.5 e Å^{-3}. Each scale division = 1 Å. The graph of bonded atoms is superimposed, with major and minor orientations indicated by solid and dashed lines, respectively. Hydrogen atoms are located at mean positions between the C_t's of the two orientations and are indicated by small dots at the intersection of dashed and solid edges. Positions of chlorine atoms (large dots) in the two orientations are seen as superposed, i.e., $d(\mathrm{Cl{-}Cl'}) = 0$.

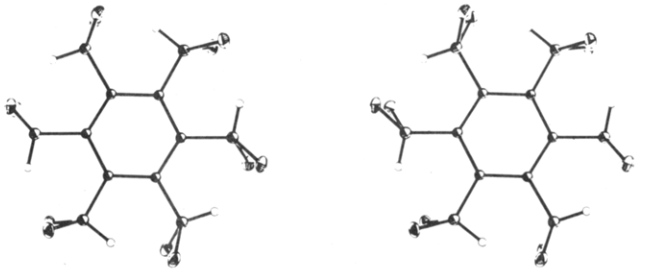

Figure 3. Stereoview of the major orientation of **2** down the approximate sixfold axis, with thermal motion ellipsoids (50% probability). The drawing is based on resolved aromatic and tertiary carbon positions resulting from the crystallographic least-squares optimizations.

about an axis perpendicular to both rings (see Figure 4 in ref 2) by an angle ϕ that is greater in **2** than in **1**.[8] The greater separation of C_{Ar} and C_{Ar}' made it possible to resolve the disorder by use of the experimental data without resorting to a geometric modeling scheme. Thus, by constraining the aromatic carbons to be isotropic, positions for the major and minor orientations (C_{Ar} and C_{Ar}', respectively) emerged in the course of the refinement (Figure 2).[9] A stereoview of the major orientation of **2** is shown in Figure 3, final atomic parameters are listed in Table I, and bond lengths, bond angles, and a torsion angle for the two orientations of **2** are compared with corresponding structural parameters of **1** in Table II. As in the case of **1**, the molecule has C_i site symmetry but the molecular parameters differ only slightly from idealized C_{6h} symmetry. As expected, values for $d(C_{Ar}{-}C_{Ar}')$, $d(C_t{-}C_t')$, and ϕ in **2**, 0.548, 1.195 Å, and 22.5°, are greater than the corresponding values in **1**,[2] 0.357, 0.769 Å, and 14.5°.

Population coefficients p and p' for the major and minor orientations of **2** were refined for the aromatic and tertiary carbons under the constraint $p + p' = 1$. The value of p, 0.6463 (35), is close to the corresponding value found for **1**,[2] 0.6748 (200). An independent determination with a crystal grown from tetrachloroethane gave a final value of $p = 0.6424$. This result suggests that the disorder ratio

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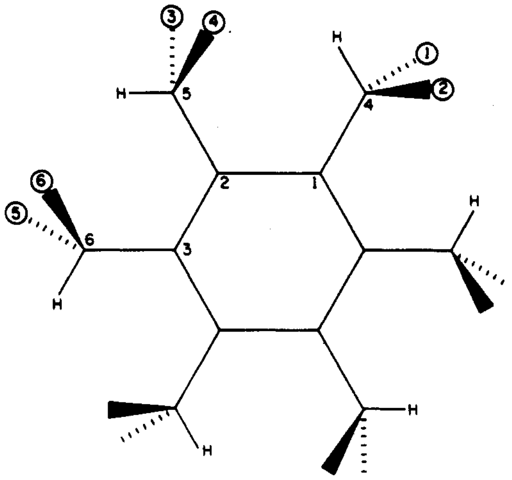
[8] This result is expected under the constraint of a rigid molecular model with standard bond lengths and angles and with idealized C_{6h} symmetry: given that the C_t–Cl bond is longer than the C_t–C_m bond, a larger ϕ is obviously required for the superposition of Cl and Cl′ in the unit cell of **2** than for the superposition of C_m and C_m' in the unit cell of **1**.

[9] Positions for C_m and C_m' had been resolved ($d(C_m{-}C_m') = 0.115$)) for **1** by use of a geometric modeling scheme that assumes the same geometry for the major and minor orientations.[2] With respect to **2** it is assumed that $d(\mathrm{Cl{-}Cl'}) = 0$ and that the two orientations need not have the same geometry.

Table I. Final Fractional Crystal Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Hexakis(dichloromethyl)benzene (2)[a]



atom	x	y	z	U
C(1)	-644 (11)	-846 (8)	-1669 (7)	9
C(2)	-1588 (11)	-1663 (7)	-834 (8)	9
C(3)	-936 (12)	-821 (9)	810 (8)	9
C(11)	24 (21)	-214 (16)	-1493 (13)	9
C(21)	-1344 (20)	-1569 (14)	-1312 (13)	9
C(31)	-1336 (20)	-1313 (14)	197 (16)	9
C(4)	-1397 (10)	-1836 (7)	-3465 (7)	13
C(5)	-3280 (11)	-3494 (7)	-1695 (7)	13
C(6)	-1911 (10)	-1647 (7)	1764 (7)	13
C(41)	-26 (19)	-499 (13)	-3190 (12)	13
C(51)	-2809 (19)	-3272 (12)	-2766 (12)	13
C(61)	-2837 (19)	-2722 (13)	444 (12)	13
Cl(1)	1054 (2)	-2018 (1)	-4264 (1)	20 (1)[b]
Cl(2)	-2891 (2)	-987 (1)	-4290 (1)	20 (1)[b]
Cl(3)	-1915 (2)	-4825 (1)	-2835 (1)	21 (1)[b]
Cl(4)	-5898 (2)	-3833 (1)	-2898 (1)	23 (1)[b]
Cl(5)	-1124 (2)	-3353 (1)	1407 (1)	24 (1)[b]
Cl(6)	-5012 (2)	-2255 (1)	1396 (1)	25 (1)[b]

[a] Standard deviations are in parentheses. For numbering of atoms, see structure above. Uncircled numerals refer to carbon atoms (major orientation) and circled numerals to chlorine atoms. Aromatic carbons: major orientation, (C_{Ar}) = C(1), C(2), C(3); minor orientation, (C_{Ar}') = C(11), C(21), C(31). Methine carbons: major orientation, (C_t) = C(4), C(5), C(6); minor orientation, (C_t') = C(41), C(51), C(61). Hydrogen parameters and anisotropic thermal parameters for chlorine are given in the supplementary material. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

p/p' is a constant for crystals of 2 obtained from heptane or tetrachloroethane, and by extension it may be inferred that it is also a constant for 1 and not a peculiarity of the individual crystal.[2]

Empirical Force-Field Calculations. It had previously been found that empirical force field (EFF) calculations satisfactorily reproduce the experimentally determined bonding parameters in 1.[2] Similarly, fair agreement was found in the present work between experimentally determined bonding parameters in 2 (Table II) and those calculated by the EFF method[10-13] and by MNDO (Table III).[14]

Table II. Comparison of Experimentally Determined (X-ray) Structural Parameters for 1 and 2[a]

		2	
atoms[b]	1[c]	major orientation	minor orientation
	Bond Lengths		
C_{Ar}–C_{Ar}	1.416	1.401 (10)	1.392 (18)
C_{Ar}–C_t	1.538	1.529 (9)	1.538 (17)
C_t–C_m/Cl	1.539	1.786 (7)	1.780 (13)
	Bond Angles		
C_{Ar}–C_{Ar}–C_{Ar}	120.0	120.0 (6)	120.0 (12)
C_{Ar}–C_{Ar}–C_t[d]	120.4	122.7 (5)	119.5 (11)
C_{Ar}–C_{Ar}–C_t[e]	119.6	117.2 (6)	120.5 (11)
C_{Ar}–C_t–C_m/Cl	115.1	111.4 (5)	112.3 (9)
C_m/Cl–C_t–C_m/Cl	113.4	110.9 (3)	111.5 (7)
	Torsion Angle		
C_{Ar}–C_{Ar}–C_t–C_m/Cl	67.4	62.3 (9)	63.3 (15)

[a] All structures averaged over C_{6h} symmetry. Average deviations in parentheses. Bond lengths in angstroms; angles in degrees. [b] C_{Ar} = aryl carbon, C_t = tertiary (methine) carbon, C_m = methyl carbon in 1. For the minor orientation of 2, C_{Ar} = C_{Ar}' and C_t = C_t'. [c] Disorder geometrically resolved.[2] Major and minor orientations are taken to have identical structures. [d] Angle anti with respect to methine hydrogen. [e] Angle syn with respect to methine hydrogen.

Table III. Structural Parameters Calculated for 2[a]

atoms	MM2[b]	MNDO[c]
	Bond Lengths	
C_{Ar}–C_{Ar}	1.419	1.434
C_{Ar}–C_t	1.538	1.530
C_t–Cl	1.792	1.799
	Bond Angles	
C_{Ar}–C_{Ar}–C_{Ar}	120.0	120.0
C_{Ar}–C_{Ar}–C_t[d]	120.1	121.4
C_{Ar}–C_{Ar}–C_t[e]	119.9	118.6
C_{Ar}–C_t–Cl	113.1	112.8
Cl–C_t–Cl	113.6	111.2
	Torsion Angle	
C_{Ar}–C_{Ar}–C_t–Cl	65.4	63.5

[a] Bond lengths in angstroms; angles in degrees. C_{Ar} = aryl carbon; C_t = tertiary (methine) carbon. [b] References 10–13. No symmetry constraint; all geometrical variables optimized. [c] Reference 14. C_{6h} symmetry assumed. [d] Angle anti with respect to methine hydrogen. [e] Angle syn with respect to methine hydrogen.

Additional EFF calculations provided useful insight into the special role played by a *complete* gearing circuit (i.e., by the presence of no fewer than six isopropyl or dichloromethyl groups on the benzene ring) in the confor-

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[10] Input geometries were based on standard bond lengths BIGSTRN-3[12] bond angles. These structures were then optimized[11] by the program BIGSTRN-3[12] with use of the MM2 force field.[13] Final structures were characterized as minima by the absence of negative eigenvalues in the matrix of analytical second derivatives.

[11] Geometry optimizations were routinely begun with the variable-metric method and concluded with the full-matrix Newton–Raphson method; analytical second derivatives were used at both stages. The final convergence criteria for the Newton–Raphson stage were as follows: rms gradient less than 10^{-6} kcal mol^{-1} Å^{-1} and rms atom movement less than 10^{-6} Å.

[12] BIGSTRN-3 (Nachbar, R. B. Jr.; Mislow, K.) is availble as QCPE No. 514 from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47405, and is described in: *QCPE Bulletin* **1986**, *6* (3), 96.

[13] Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395. Two modifications were used for C_{Ar}–C_{Ar} bonds, l° = 1.3937 Å and k_s = 8.0667 mdyn Å^{-1}. All torsional parameters for C_{Ar} were taken to be the same as for C(sp^2). See: Ōsawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 7475. Bond angle parameters for C_{Ar}–C(sp^3)–Cl were taken to be the same as for C(sp^3)–C(sp^3)–Cl. Test calculations on 1,2,3,4-tetrachloro- and 1-phenyl-1,2,3,4-tetrachlorotetralin gave generally satisfactory agreement with the experimentally determined values (Godfrey, J. E.; Waters, J. M. *Cryst. Struct. Commun.* **1973**, *2*, 677; **1975**, *4*, 45).

[14] The only significant discrepancy from the experimental geometrical parameters was found for C_{Ar}–C_{Ar} bond lengths: as calculated by MNDO, these are about 0.03–0.04 Å longer than observed. This is, however, consistent with a general tendency of the MNDO method to overestimate C_{Ar}–C_{Ar} bond lengths in aromatic compounds. See: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. The program used is described by: Bischof, P.; Friedrich, G. *J. Comput. Chem.* **1982**, *3*, 486.

mational stabilization of 1 and 2. According to these calculations, α,α-dichloromethylbenzene, like isopropylbenzene,[15] adopts the "bisected" C_s ground-state conformation in which the methine hydrogen lies in the benzene plane. The ground-state conformation of 1,2-bis(dichloromethyl)benzene also has C_s symmetry, with the dichloromethyl groups gear-meshed as well as bisected. However, another conformation with C_2 symmetry, in which the two methine hydrogens face each other at a slight angle ($\theta(C_{Ar}–C_{Ar}–C_t–H) = 23.8°$), corresponds to an energy minimum that lies only 1.2 kcal mol^{-1} above the ground state. The strong implication is that the driving force for static gearing in vicinal dichloromethyl or isopropyl[16] groups, i.e., the energetic preference for conformations in which the methine hydrogen of one group is tucked into the cleft formed by the two methyls or chlorines of the neighboring group, is of marginal importance in the absence of buttressing substituents in neighboring positions. This implication is clearly borne out in the case of 1,2-diisopropylbenzene, a compound in which the relationship described for the conformers of 1,2-bis(dichloromethyl)benzene is almost exactly reversed: the ground-state conformation now has C_2 symmetry, with the two methine hydrogens facing each other ($\theta = 26.4°$), while the gear-meshed C_s conformation corresponds to a minimum that lies 1.7 kcal mol^{-1} above the ground state.[17,18] Thus, the energetic preference for static gearing, if any, is very slight so long as space is available around the ring periphery for the accommodation of the bulky R groups in the CHR_2 side chains, i.e., so long as at least one position on the benzene ring remains unsubstituted. Consider, for example, pentakis(dichloromethyl)benzene, whose ground-state conformation has C_s symmetry and in which the dichloromethyl groups are fully geared, with the methine hydrogens in the terminal 1- and 5-positions pointing toward the C_{Ar} hydrogen in the 6-position and toward the dichloromethyl group in the 4-position, respectively. Rotation of the dichloromethyl group in the 5-position leads to a conformational minimum that lies 9.7 kcal mol^{-1} above the ground state. In this conformation, the methine hydrogens in the 1- and 5-positions face each other across the "gap" in the 6-position, while there is an unavoidable clash between the two pairs of chlorine atoms facing each other in the vicinal 4- and 5-positions. By contrast, similar rotation of the dichloromethyl group in the 1-position leads to a conformational minimum that lies only 1.6 kcal mol^{-1} above the ground state: in this conformation the methine hydrogens now face each other in the 1- and 2-positions, while the two pairs of chlorine atoms facing each other in the 1- and 5-positions are well separated by the gap in the 6-position and straddle the C_{Ar} hydrogen. Once again the relationship described above is almost exactly reversed by substitution of isopropyl for dichloromethyl: the methine hydrogens in the 1- and 2-positions of pentaisopropylbenzene face each other in the ground state, which is 2.0 kcal mol^{-1} *more* stable than the gear-meshed C_s conformation. However, rotation of the isopropyl group in the 5-position of the latter leads to a conformational minimum that lies 13.5 kcal mol^{-1} above the ground state.

Evidently it is the destabilizing effect of gear-clashing repulsion between pairs of methyls or chlorines in vicinal isopropyl or dichloromethyl groups that is the principal conformational determinant in polyisopropyl or poly(dichloromethyl)benzenes, rather than the stabilizing effect of gear-meshing. In the hexasubstituted compounds 1 and 2, all but one (C_{6h}) of the conformations are destabilized by repulsion between pairs of methyls or chlorines on neighboring groups. It is thus recognized that 1 is unique among vicinally substituted polyisopropylbenzenes in having a ground-state conformation with homodirectional isopropyl groups.[19]

The difference of 12.3 kcal mol^{-1} in steric energy between the calculated C_{6h} ground state of 2 (R_0) and the conformational isomer with one dichloromethyl group turned by 146° (R_1) is the same as the difference in steric energy previously calculated for the corresponding conformational isomers of 1.[2] Indeed, the topomerization sequence ($R_0 \rightarrow R_1 \rightarrow R_{12} \rightarrow R_{126} \rightarrow R_{1256} \rightarrow R_{12356} \rightarrow R_{123456}$) is found to be identical with the one calculated for 1, and the overall calculated barriers are extremely close (33.9 kcal mol^{-1} for 2 vs. ca. 35 kcal mol^{-1} for 1[2]). The close similarity found for the molecular structures of 1 and 2 is thus extended into the dynamic domain.

Experimental Section

Hexakis(dichloromethyl)benzene (2).[20] A slow stream of chlorine gas was bubbled through a refluxing solution of hexamethylbenzene (0.15 g) in 30 mL of carbon tetrachloride, while the reaction mixture was irradiated with a 150-W lamp. After 30 h the reaction mixture was cooled, and the solid that had deposited in the flask and gas inlet was collected. The product (0.20 g, 37%) was essentially pure by NMR. Recrystallization from tetrachloroethane afforded pure 2: mp >300 °C; ^{1}H NMR (250 MHz, CCl_4) δ 8.30 (s) (lit.[5] δ 8.35, lit.[7] δ 8.32 ($CDCl_3$)).

X-ray Crystallography. Crystals of 2 were obtained from heptane by slow evaporation at room temperature. A crystal of approximately $0.15 \times 0.20 \times 0.35$ mm^3 was chosen for the X-ray measurements. Crystal data: $C_{12}H_6Cl_{12}$, M = 575.44 g mol^{-1}; triclinic (space group $P\bar{1}$ assumed throughout); a = 6.248 (1) Å, b = 9.749 (3) Å, c = 9.763 (2) Å, α = 116.32 (2)°, β = 94.97 (2)°, γ = 108.20 (2)°, V = 488.4 (2) Å^3, d_{calc} = 1.956 g cm^{-3}, Z = 1. X-ray intensities were collected at 175 K on a Nicolet R3m four-circle diffractometer equipped with a nitrogen-flow cooling device applying Cu Kα radiation (λ = 1.54178 Å). A total of 1368 independent reflections were recorded with $3° \leq 2\theta \leq 114°$ of which 1159 with $|F_0| > 3\sigma(F_0)$ were considered unique and observed. The structure was solved by direct methods using the SHELXTL software. The chlorine atoms were refined anisotropically, and the carbon and hydrogen atoms were refined isotropically by using a block cascade least-squares procedure. Hydrogen atoms were included at ideal positions (C–H = 0.96 Å and C–C–H = 109.5°) for all methine carbon atoms, and a single hydrogen with a site occupancy of 1.0 was fixed at the average position between neighboring hydrogens at major and minor positions, H and H′, respectively. Population coefficients p and p' were refined for the aromatic carbons, C_{Ar} and C_{Ar}', and the tertiary carbons, C_t and C_t', of the major (unprimed) and minor (primed) orientations, with the constraint $p + p' = 1$; the final value of p was 0.6463 (35). R and R_w factors after the refinement were 0.041 and 0.052, respectively.

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(15) Weissensteiner, W.; Gutiêrrez, A.; Radcliffe, M. D.; Siegel, J.; Singh, M. D.; Tuohey, P. J.; Mislow, K. *J. Org. Chem.* **1985**, *50*, 5822 and references therein.

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

(17) The C_{2v} conformation with $\theta = 0°$ in which the methine hydrogens face each other is a statiomer with two negative eigenvalues and a steric energy of 0.8 kcal mol^{-1} relative to the ground state.

(18) NMR evidence suggests the presence of similar conformers in 3,4-diisopropyl-5-methylthiazole derivatives. See: Lidên, A.; Roussel, C.; Chanon, M.; Metzger, J.; Sandström, J. *Tetrahedron Lett.* **1974**, 3629.

(19) An analogous situation is encountered in tetraisopropylethylene. While this molecule is statically geared (C_{2h} symmetry), the corresponding gear-meshed structures in triisopropylethylene are calculated to lie 0.92 and 1.16 kcal mol^{-1} *above* a conformation in which the methine hydrogens of the vicinal isopropyl groups point toward each other. See: Casalone, G.; Pilati, T.; Simonetta, M. *Tetrahedron Lett.* **1980**, *21*, 2345. Pettersson, I.; Berg, U. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1365.

(20) Procedure of Mark and Pattison[7] (Mark, V., private communication). Imhof's procedure,[5] similar except for the use of tetrachloroethane as solvent, yields appreciable quantities of hexachloroethane as a byproduct of the chlorination.

Acknowledgment. We thank the National Science Foundation (CHE-8510067) for support of this work and Donna Van Engen for a helpful discussion.

Registry No. 1, 800-12-4; 2, 33624-92-9; hexamethylbenzene, 87-85-4.

Supplementary Material Available: Bond lengths and bond angles, with standard deviations, for 2 (Tables IV and V), final anisotropic thermal parameters for chlorine (Table VI), and atomic parameters for hydrogen (Table VII) (3 pages). [The structure factor table is available from the author.] Ordering information is given on any current masthead page.

Neighboring Group Participation in Radicals: Pulse Radiolysis Studies on Radicals with Sulfur–Oxygen Interaction

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Neighboring group participation by alcohol and carboxylate groups resulting in kinetic and thermodynamic stabilization of an oxidized sulfur atom in various organic sulfides is reported. The resulting radical intermediates of the general type $(-\overline{\mathrm{S}\leftrightarrow\mathrm{O}})^{\bullet}$ are characterized by an optical absorption in the 400-nm range and exhibit lifetimes of up to several hundred microseconds in aqueous solution under pulse radiolysis conditions. Significant sulfur–oxygen interaction seems to occur, however, only if both heteroatoms are separated by three or four carbon atoms in the unoxidized molecule which enables favorable five- or six-membered ring structures in the radical intermediates. This geometric effect can additionally be favored by minimizing the free rotation of the functional groups through rigid molecular structures, e.g., in norbornane derivatives, and introduction of particular substituents. A most suitable function for stabilization of an oxidized sulfur atom seems to be a carboxylate group where an overall neutral radical of the general structure $-\overline{\mathrm{S}^{\bullet+}\leftrightarrow{}^{-}\mathrm{O}}\mathrm{OC}$ is formed. In these species stabilization can be envisaged to involve the carboxylate group as a whole rather than only an individual oxygen atom. The bond strength of the sulfur–carboxylate interaction is estimated to be of the order of 50 kJ mol^{-1} as deduced from the temperature dependence of its dissociation. Further evidence for net sulfur–carboxylate bonding is provided by rate constants of 10^5–10^7 M^{-1} s^{-1} for its proton-assisted decay. These rates are considerably lower than for the diffusion controlled protonation of free carboxylate functions. Oxidation of *endo*-2-(2-hydroxyisopropyl)-*endo*-6-(methylthio)bicyclo[2.2.1]heptane yields a transient where sulfur–oxygen interaction is associated with a strong acidification of the alcoholic hydroxyl group. A p*K* = 5.9 has been measured for the $(-\overline{\mathrm{S}\leftrightarrow\mathrm{O}}\mathrm{H})^{\bullet+} \rightleftharpoons (-\overline{\mathrm{S}\leftrightarrow\mathrm{O}})^{\bullet} + \mathrm{H}^+$ equilibrium. All the results on these transient radical intermediates can be viewed in terms of neighboring group participation. Such participation is also clearly evidenced in the formation and properties of intermolecular radical cations, $(\mathrm{R_2S\therefore SR_2})^+$, derived from these sulfides, and in the kinetics of the primary oxidation process. Absolute rate constants for the one-electron oxidation of various sulfides by $\mathrm{CCl_3OO^{\bullet}}$ radicals, for example, have been found to range from 3×10^8 to $<10^{-6}$ M^{-1} s^{-1} depending on the nature of the oxygen containing functional groups. The present results are finally discussed in terms of the general possibility of stabilization of an oxidized sulfur function by other heteroatoms. Several electronic structures including the two-center-three $(2\sigma/1\sigma^*)$ electron bond can be advanced to describe the physicochemical properties of the radicals with sulfur–oxygen interaction.

Introduction

In previous studies[1-7] we have shown that radical cations of the general type $\mathrm{R_2S^{\bullet+}}$ can be generated in the radical-induced oxidation of organic sulfides. It has also been demonstrated that these sulfur-centered radical species exhibit a high tendency to stabilize themselves by reaction with an unoxidized sulfide molecule. This occurs within

$$\mathrm{R_2S^{\bullet+} + R_2S \rightleftharpoons (R_2S\therefore SR_2)^+} \qquad (1)$$

a thermodynamic equilibrium and leads to the formation of an intermolecular sulfur–sulfur bond containing a total of three electrons (eq 1). The latter results from interaction of the single p-electron in $\mathrm{R_2S^{\bullet+}}$ with the p-electron pair of the unoxidized $\mathrm{R_2S}$. The $\mathrm{S\therefore S}$ bond contains two electrons in a bonding σ-orbital and one electron in an antibonding σ*-orbital.

Considering the nature of the three-electron bond it is not surprising to see such bonds also being formed intramolecularly, e.g., from dithia compounds,[2,4,7-12] or with participation of other heteroatoms.[9,13-26] Several recent

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(1) Bonifačić, M.; Möckel, H.; Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1975**, 675.

(2) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436.

(3) Göbl, M.; Bonifačić, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5984.

(4) Bonifačić, M.; Asmus, K.-D. *J. Org. Chem.* **1986**, *51*, 1216.

(5) Mönig, J.; Goslich, R.; Asmus, K.-D. *Ber. Bunsenges. Phys. Chem.* **1986**, *90*, 115.

(6) Asmus, K.-D. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1986**, *31*, 870.

(7) Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H.; Veltwisch, D. *J. Am. Chem. Soc.* **1979**, *101*, 5322.

(8) Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1975**, 238.

(9) Asmus, K.-D.; Bahnemann, D.; Bonifačić, M.; Gillis, H. A. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 213.

(10) Musker, W. K.; Wolford, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3055.

(11) Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416.

(12) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryan, M. D.; Musker, W. K. *J. Am. Chem. Soc.* **1979**, *101*, 1040.

(13) Symons, M. C. R.; Petersen, R. L. *J. Chem. Soc., Faraday Trans. 2* **1978**, 210.

(14) Bonifačić, M.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1980**, *2*, 758.

(15) Hiller, K.-O.; Asmus, K.-D. *Int. J. Radiat. Biol.* **1981**, *40*, 583.

(16) Packer, J. E. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1015.

(17) Musker, W. K.; Hirshon, A. S.; Doi, J. T. *J. Am. Chem. Soc.* **1978**, *100*, 7754.

0022-3263/87/1952-3717$01.50/0