J. Am. Chem. Soc. **1989**, *111*, 4583–4586

Matrix IR Spectrum and ab Initio SCF Calculations of Molecular SiS_2

Hansgeorg Schnöckel* and Ralf Köppe

Contribution from the Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster, West Germany. *Received August 29, 1988*

Abstract: In solid argon molecular SiS_2 is generated by a reaction of SiS with S atoms. The antisymmetric stretching vibration ν_{as}(SiS) is observed at 918 cm^{-1}. Bonding and structure (force constants from experimentally observed frequencies and results from ab initio SCF calculations) of SiS_2 are compared with that of the similar molecules: CO, CS, CO_2, COS, CS_2, SiO, SiS, SiO_2, and SiOS.

Compounds containing SiX multiple bonds have been investigated intensively recent years.[1] There are on the one hand "stable" compounds, which are stabilized by bulky ligands to prevent, e.g., polymerization; on the other hand, there are more simple compounds, which can be stabilized under extreme conditions, e.g., in solid noble gases (matrix isolation technique). The latter ones are especially interesting from a theoretical point of view, since their SiX bond is hardly influenced by other effects, e.g., steric factors. Additionally for these species reliable quantum chemical calculations can easily be performed, and subsequently these results can be compared with the experimental ones. Under this aspect we have prepared several species containing SiX double bonds in recent years under matrix conditions: SiO_2,[2] SiOS,[3] $SiOF_2$,[4] $SiOCl_2$,[5] and AgSiO.[6] In this paper we characterize SiS_2, which was the missing species in the series SiO_2, SiOS, and SiS_2. SiX double bonds (X = O, S) in SiX_2 molecules are compared with CS and CO bonds in the analogous carbon-containing species.

Technical Details

Matrix Isolation and Spectroscopy. SiS is generated when H_2S is passed over heated Si (Wacker) at about 1500 K in an Al_2O_3 furnace. Together with SiS, a mixture of Ar/COS (200:1) is co-condensed for about 30 min on a helium-cooled Cu surface. The setup with the flow cryostat has been described before.[7–9] The IR spectra were recorded in transmission with a reflection unit using a Bruker 113v FT IR spectrometer. Irradiation for photolysis has been performed with a medium pressure Hg lamp (only H_2O filter).

Details of Computation. Ab initio SCF computations were performed for the electronic ground states of CO, CS, SiO, SiS, SiO_2, SiOS, SiS_2, CO_2, COS, and CS_2 by using the Karlsruhe version[10] of the Columbus system of programs.[11,12] A gradient program[13] was used for geometry optimization.

The following CGTO basis was used:

$$\begin{array}{lll} \mathrm{C} & (9,5,1)/[5,3,1] & \eta(d) = 0.8 \\ \mathrm{O} & (9,5,1)/[5,3,1] & \eta(d) = 1.0 \\ \mathrm{Si} & (11,7,1)/[6,4,1] & \eta(d) = 0.4 \\ \mathrm{S} & (11,7,1)/[6,4,1] & \eta(d) = 0.55 \end{array}$$

The parameters of s and p CGTO basis functions were taken from Huzinaga's tables.[14] The basis is of double-ζ potential quality, or better, which on the SCF level usually gives geometric structure constants with errors of about 1–2° or pm.

Table I. Observed and Calculated[a] Frequencies[c] of SiS_2

isotopomer	obsd	calcd
$^{28}5Si^{32}S_2$	917.96	917.96
$^{29}Si^{32}S_2$	906.99	906.98
$^{30}Si^{32}S_2$	896.51	896.58
$^{28}Si^{32}S^{34}S$	913.98	914.03[b]
$^{28}Si^{34}S_2$		909.78

[a] Corrected for anharmonicity.[21] f(SiS) − f(SiS/SiS) = 4.83 mdyn/Å. [b] In this calculation ($C_{\infty v}$ symmetry) the second stretching vibration varies between 504 and 524 cm^{-1} (cf. text). [c] In units of cm^{-1}.

Table II. Force Constants[a] and Bond Energies[b] of Linear XY and XYZ Molecules

molecule X=Y=Z	f(XY)	f(YZ)	f(XY/YZ)	bond energy (cf. text)	lit.
O=C	18.6			1071.8	23, 26
S=C	8.5			708.8	23, 26
O=C=O	15.6		1.43	799.0	24, 26
O=C=S	15.7	7.2	1.1		26
S=C=S		7.67	0.70	572.3	24, 26
O=Si	9.1			794.1	23, 26
S=Si	5.0			615.8	23, 26
O=Si=O	9.2		0.4	621.7	2, 26
O=Si=S	9.0	4.86	0.2		3
S=Si=S				533.1	

[a] In units of mdyn/Å. [b] In units of kJ/mol.

The electronic structure was visualized by means of a population analysis based on occupation numbers.[15–17] Within this approach the electronic structure is characterized by atomic net charges Q(A) for atom A and the shared electron number SEN(AB) for the AB bond.[18]

Results

After co-condensation of SiS with COS and Ar in the proportions 1:1:500 on a helium-cooled surface, the IR spectrum shows mainly the absorptions of SiS and COS. The following frequencies are in line with those given in the literature:[19] $^{28}Si^{32}S$, 739.09 cm^{-1}; $^{29}Si^{32}S$, 732.34 cm^{-1}; $^{28}Si^{34}S$, 728.97 cm^{-1}; $^{30}Si^{32}S$, 725.96 cm^{-1}.

Figure 1a illustrates the 720–750-cm^{-1} region of the IR spectrum and shows that there are additionally two bands at 727.4 and 724.5 cm^{-1} (marked with asterisks), which have to be assigned

---

(1) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(2) Schnöckel, H. *Angew. Chem.* **1978**, *90*, 638; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 616.

(3) Schnöckel, H. *Angew. Chem.* **1980**, *92*, 310; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 323.

(4) Schnöckel, H. *J. Mol. Struct.* **1980**, *65*, 115.

(5) Schnöckel, H. *Z. Anorg. Allg. Chem.* **1980**, *460*, 37.

(6) Mehner, T.; Schnöckel, H.; Almond, M. J.; Downs, A. J. *J. Chem. Soc., Chem. Commun.* **1988**, 117.

(7) Becher, H. J.; Schnöckel, H.; Willner, H. *Z. Phys. Chem.* (*Munich*) **1974**, *92*, 33.

(8) Ahlrichs, R.; Ehrhardt, C.; Lakenbrink, M.; Schunck, S.; Schnöckel, H. *J. Am. Chem. Soc.* **1986**, *108*, 3596.

(9) Schnöckel, H. *Z. Anorg. Allg. Chem.* **1980**, *460*, 37.

(10) Ahlrichs, R.; Boehm, H. J.; Erhardt, C.; Scharf, P.; Schiffer, H.; Lischka, H.; Schindler, M. *J. Comput. Chem.* **1985**, *6*, 200.

(11) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111. Rys, J.; Dupuis, M.; King, H. F. *J. Comput. Chem.* **1983**, *4*, 154.

(12) Pitzer, R. M. *J. Chem. Phys.* **1973**, *58*, 3111.

(13) Schaefer, H. F.; Pitzer, R. M., private communication to R. Ahlrichs.

(14) Huzinaga, S. *Approximate Atomic Functions. Technical Report 1971*; University of Alberta, Canada.

(15) Davidson, E. R. *J. Chem. Phys.* **1967**, *46*, 3320. Roby, K. R. *Mol. Phys.* **1974**, *27*, 81.

(16) Heinzmann, R.; Ahlrichs, R. *Theor. Chim. Acta* **1976**, *42*, 33.

(17) Erhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231. Ahlrichs, R.; Ehrhard, C. *Chem. Unserer Zeit* **1985**, *19*, 120.

(18) The SEN provides a reliable measure of the covalent bond strength. To give the idea of typical values found for SEN, we list some representative cases: strong bonds such as C–C or C–H (SEN = 1.4); double bonds such as C=C (SEN = 2.2); triple bonds such as C≡C or N≡N (SEN = 3.3). A reduced SEN is found for polar bonds as in NaF (SEN = 0.3) and for weak bonds such as in Cl_2 (SEN = 0.9) and in F_2 (SEN = 0.6).

(19) Atkins, R. M.; Timms, P. L. *Spectrochim. Acta* **1977**, *33A*, 853.

0002-7863/89/1511-4583$01.50/0

Table III. Results of ab Initio Calculations and Population Analyses

molecule X=Y=Z	total energy, au	r(XY), pm	r(YZ), pm	Q(X)	Q(Y)	Q(Z)	SEN(XY)	SEN(YZ)
O=C	−112.768 482	110.6		−0.063	0.063		2.57	
S=C	−435.291 383	151.9		0.131	−0.131		2.52	
O=C=O	−187.687 108	113.6	113.6	−0.341	0.682	−0.341	2.13	2.13
O=C=S	−510.270 869	112.5	157.2	−0.213	0.422	−0.209	2.27	1.88
S=C=S	−832.849 978	154.7	154.7	−0.075	0.150	−0.075	2.08	2.08
O=Si	−363.812 078	148.9		−0.340	0.340		2.47	
S=Si	−686.417 118	191.5		−0.164	0.164		2.43	
O=Si=O	−438.658 924	148.3	148.3	−0.610	1.219	−0.610	1.89	1.89
O=Si=S	−761.298 800	148.5	190.3	−0.593	0.972	−0.378	1.92	1.95
S=Si=S	−1083.937 267	190.7	190.7	−0.356	0.713	−0.356	1.98	1.98

to associates between SiS and COS, since they decrease after irradiation, while new absorptions growing in the 900-cm^{-1} region are observed (Figure 1b). Simultaneously the intensity of the CO absorption (at 2140 cm^{-1}) increases, while that of COS (ν(CO) at 2049 cm^{-1}) is diminished. Thus it can be concluded that S atoms[20] have been produced and have reacted with the carbene analogue molecule SiS to generate SiS_2.

The antisymmetric stretching vibration of a linear SiS_2 molecule is expected in the region of 900 cm^{-1}. Therefore we assign the new bands near 900 cm^{-1} to isotopomers of SiS_2 (Figure 1b). The observed splitting pattern is in accordance with this assignment. The accurate frequencies for the isotopomers are listed in Table I. Simple force constant calculations for this species with $D_{\infty h}$ symmetry also confirm this assignment (Table I). After corrections for the different anharmonicity[21] of the isotopomers the experimental frequency shift is in excellent agreement with the calculated one. This is only true for a bond angle of 180°. Calculations on the basis of smaller bond angles produce significant smaller frequency shifts than those obtained experimentally. From the frequencies the symmetry force constant $F = f_{(\mathrm{SiS})} - f_{(\mathrm{SiS/SiS})}$ is calculated to be 4.83 mdyn/Å. Inspection of the interaction force constants of the molecules CO_2, COS, CS_2, SiO_2, and SiOS (cf. Table II) suggests that for SiS_2 this constant is expected to be in the range 0–0.2 mdyn/Å. With the help of this plausible assumption the symmetric stretching vibration, which is not observed in the IR spectrum, can be calculated to be 514 ± 15 cm^{-1}. The deformation vibration should be observed between 180 and 260 cm^{-1}. But due to its expected low intensity it could not be detected. The isotopomer $^{28}Si^{32}S^{34}S$ is of lower symmetry than the isotopomers with $D_{\infty h}$ symmetry. Thus there should be an interaction between the two stretching vibrations. This is in accordance with experiment: the observed infrared absorption for $^{28}Si^{32}S^{34}S$ (Table I) is not in the middle of those of the $D_{\infty h}$ species containing respectively two ^{32}S or two ^{34}S atoms. On the other hand the calculated position of the infrared absorption of $^{28}Si^{32}S^{34}S$ is in excellent agreement with the experimental position (Table I), when the predicted value for the symmetric stretching vibration (514 ± 15 cm^{-1}) is included in the calculation. This is additional confirmation for the correct assignment of our observed absorptions to the SiS_2 molecule. Besides these experiments we vaporized solid SiS_2 to get matrix spectra of molecular SiS_2. By this method gaseous SiS_2 has been produced and detected by means of mass spectrometry[22] although the principal vapor-phase product is SiS. Although we observed a weak absorption at 918 cm^{-1} in these experiments, which is further confirmation of our correct interpretation, these spectra are not of comparable quality (no pronounced isotopic splitting) with those discussed above. Furthermore there are some other absorptions of medium intensity that have to be attributed mainly to reaction products of SiS_2 in the furnace (e.g., hydrolysis).

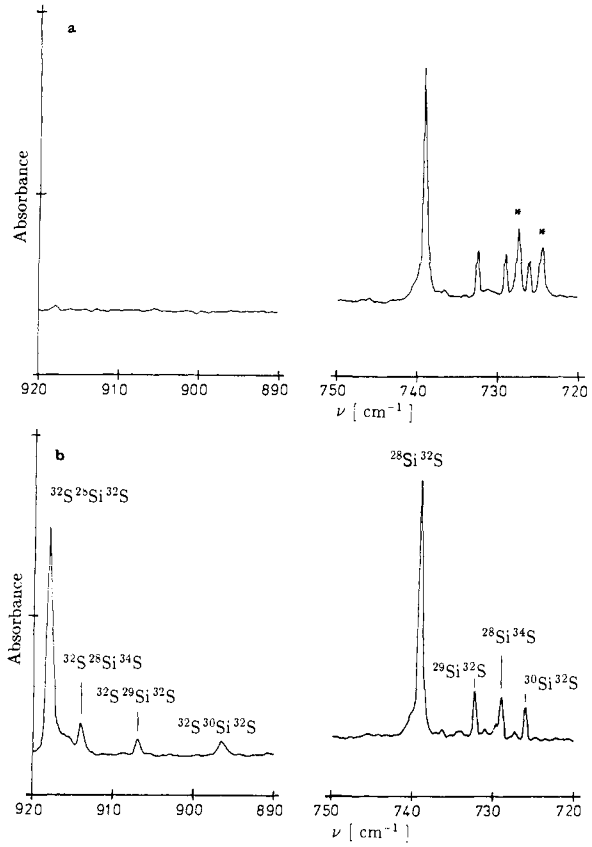

Figure 1. Sections of the IR spectra of SiS co-condensed with COS in an Ar matrix (a) before and (b) after photolysis (cf. text).

The results of our quantum chemical calculations are listed in Table III. They are discussed in the next section.

Discussion

To interpret our results on SiS_2, we have to compare them with those of similar molecules. Thus stretching and interaction force constants and bond energies of some carbon and silicon compounds containing O and/or S are listed in Table II. These experimental results have to be compared with those obtained from ab initio SCF calculations, which have been performed under similar conditions to visualize trends in bonding. Values of energy, bond distance, SENs, and charges are listed in Table III.[25]

Diatomics. By inspection of the force constants of the diatomics (Table II) it can be seen that bonds between elements of the second period are the strongest ones (f(CO)). Force constants decrease when one element of the third period is involved (f(SiO)f(CS)). Finally the lowest force constant is observed in the molecule SiS

---

(20) Hawkins, M.; Almond M. J.; Downs, A. J. *J. Phys. Chem.* **1985**, *89*, 3326.

(21) Becher, H. J. *Fortschritte der chemischen Forschung*; Springer: Berlin, 1968; Vol. 10.

(22) Mills, K. C. *Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides*; Butterworths: London, 1974.

(23) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.

(24) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*; Springer-Verlag: Berlin, 1966.

(25) Though most of these molecules have been investigated by ab initio computations, we have had to perform additional calculations under comparable conditions, to visualize trends in bonding.

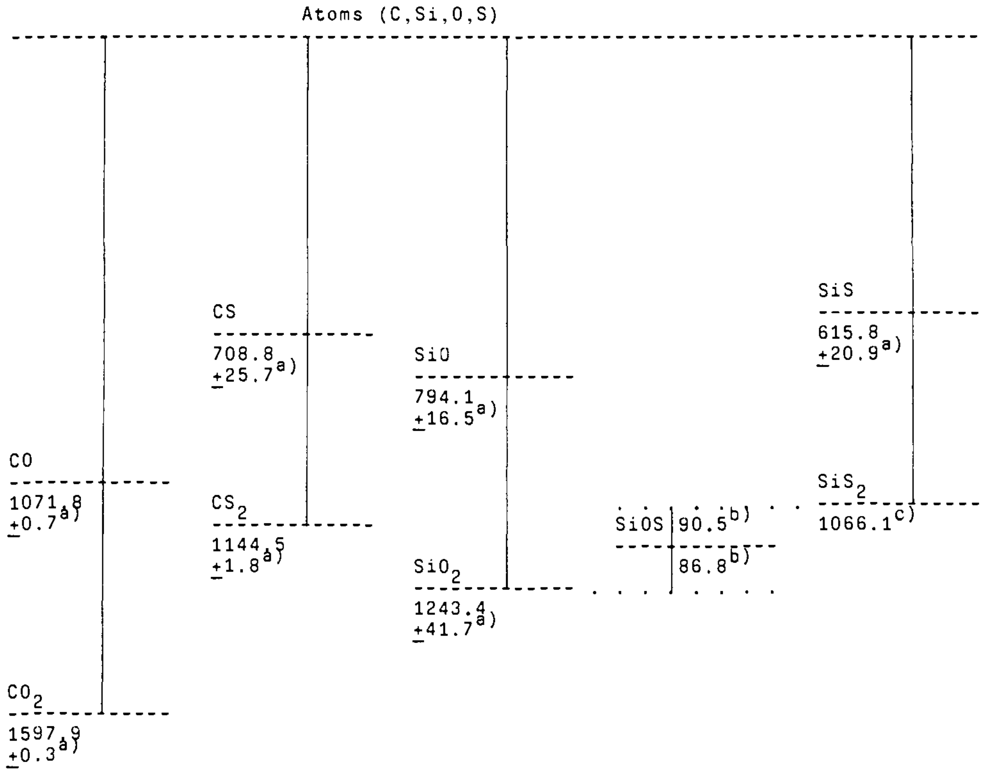

Figure 2. Atomization energies obtained by experimental (a) and theoretical investigations (kJ/mol and 0 K): (a) Reference 26. (b) $\Delta H^{at}(SiO)^a - \Delta H^{at}(SiS)^a - \Delta\Delta_R H^{SCF}$. $\Delta\Delta_R H^{SCF}$: Difference of reaction energies of $SiO + O \rightarrow SiO_2$ and $SiS + O \rightarrow SiOS$, $\Delta\Delta_R H^{SCF} = 91.5$ kJ/mol, and of $SiO + S \rightarrow SiOS$ and $SiS + S \rightarrow SiS_2$, $\Delta\Delta_R H^{SCF} = 87.8$ kJ/mol; obtained from SCF calculations under neglect of zero-point effects. (c) Obtained from the other values of this table; the value of 915.7 kJ/mol, obtained by Drowart[22] seems to be too small.

containing two atoms of the third period.

Also the values of bond energy[26] reflect the decrease in bond strength in the direction $CO \rightarrow SiO \rightarrow CS \rightarrow SiS$.

These trends are not accompanied by equivalent differences in the SENs. As SENs are a measure of covalent bond strength, there are only small variations for the molecules CO, SiO, CS, and SiS (Table III). The most significant difference between carbon and silicon compounds under discussion is the increase of ionic character for the latter ones, which may be also one reason for their higher reactivity. Anyway it can be seen that the decrease in covalent bond strength for the Si-containing species is accompanied, as expected, by growing ionic contributions.

Triatomics. All correlations of bonding given above for the diatomic species are also true for the triatomics. So in the pairs CO_2–SiO_2 and COS–SiOS charges at silicon are about twice those at carbon. A different relation is observed only between CS_2 and SiS_2: There are nearly nonpolar CS bonds, whereas SiS bonds exhibit the expected polarity.[27] Most interesting of all is a comparison between the diatomic and triatomic molecules, since bonds should be significantly weakened going from triple- to double-bonded systems. We will discuss the following pairs of molecules:

$$CO \rightarrow CO_2 \ (1) \qquad CS \rightarrow CS_2 \ (2)$$

$$SiO \rightarrow SiO_2 \ (3) \qquad SiS \rightarrow SiS_2 \ (4)$$

Bond energies, SENs, force constants, and distances of the XY_2 species relative to those of the XY molecules are listed in Table IV. The first important finding is that, with respect to force constants and distances, for the SiO and SiS systems there are nearly no differences between double and triple bonds. Larger differences between these bonding parameters are observed in similar carbon-containing compounds. Especially the ratio of the force constants for CO_2/CO demonstrates that there is a strong triple bond in CO. Since both parameters (*f*, *r*) characterize a bond near the equilibrium distance, one has to conclude that, at least in this bonding region, SiO and SiS double and triple bonds are very similar, while there are small but significant differences between CX multiple bonds.

Table IV. Relative Bond Energies, SENs, Force Constants, and Distances

	CO_2/CO	CS_2/CS	SiO_2/SiO	SiS_2/SiS
bond energy	0.75	0.81	0.78	0.87
SEN	0.83	0.83	0.77	0.82
f(XY)	0.84	0.90	1.0	1.0
$1/d$	0.97	0.98	1.0	1.0

At large distances a bond can be characterized by the bond energy. Thus the knowledge of accurate values of bond energy would help to understand bonding in these molecules. Unfortunately, even for molecular SiO_2, this value has a very large error (±33 kJ/mol[26]), but nevertheless the following rough calculation can be performed: The listed ΔH values[26] for the molecules SiO, SiO_2, and SiS together with the results from our ab initio calculations allow us to estimate the differences in stability, which are shown in the Figure 2.

The listed values are the atomization energies of the molecules (kJ/mol). Since these values are based on experimental and theoretical results which exhibit to some extent a large error, they can show only trends in bonding. However, they demonstrate that for SiS_2, which is of most interest in this paper, the atomization energy is much higher (1066 kJ/mol) than assumed until now (916 kJ/mol[22]).

The bond energies of all double- and triple-bonded systems under discussion are compared in Table IV: As expected, the difference between double and triple bonds decreases in the following directions:

$$C/O \rightarrow C/S \qquad Si/O \rightarrow Si/S$$

$$C/O \rightarrow Si/O \qquad C/S \rightarrow Si/S$$

This difference between double- and triple-bond energies reaches

---

(26) Chase, Jr., M. W.; Davies, C. A.; Downey, Jr., J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *Janaf Thermochemical Tables*, 3rd ed.; American Chemical Society: Midland, 1985.

(27) The nonpolar bonds in CS_2 are expected, since the electronegativities of C and S are nearly equal.

a minimum for the SiS compounds. This trend will probably be more pronounced in similar Ge- and Sn-containing species. Hence it follows that a strong triple bond is found only in CO.

Ahlrichs showed a direct connection between SENs and bond energy.[17] This connection is also true for the molecules under discussion if one compares only the carbon- or the silicon-containing species. Furthermore, differences between double and triple bonds are smaller in the sulfides.

On the other hand, with respect to SENs, silicon compounds show unexpectedly larger differences between double and triple bonds than the analogous carbon-containing species. This demonstrates that the SENs for SiX_2 molecules are particularly small. The reason appears to be that the SiX_2 molecules show stronger ionic contributions to bonding, and this, in turn, is equivalent to weaker covalent bonding.

Conclusion

The molecule SiS_2 has been characterized by matrix IR investigation and by ab initio SCF calculations. With the help of these data, double and triple bonds in the systems C/O, C/S, Si/O, and Si/S are compared. The following trends can be deduced:

Bond parameters, which characterize a bond near the equilibrium position (bond distance and stretching force constant), exhibit significant differences only between double and triple bonds for the C/O system. The expected differences between the two multiple bonds are best described by bond energies, which characterize bonds at large distances. The SENs, which represent the covalent bonding contributions, are useful only to distinguish double and triple bonds, when ionic bonding is of comparable size in each. Therefore, in this respect, the more ionic silicon-containing molecules cannot be directly compared with the analogous carbon compounds.

Anyway, this discussion is an impressive example of the well-known fact that a bond cannot be described by a single parameter. A complete description can be given only by the whole potential function.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and in part by the Fonds der Chemischen Industrie. We thank M. Almond for corrections to the English text.

Registry No. SiS_2, 13759-10-9.

Systematic Effects of Crystal-Packing Forces: Biphenyl Fragments with H Atoms in All Four Ortho Positions

Carolyn Pratt Brock* and Robin P. Minton

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055. *Received July 18, 1988*

Abstract: A comparison of observed and calculated distribution functions for the twist angle around the central C–C bond of biphenyl fragments with H atoms in all four ortho positions has been made. Reliable sets of coordinates for 101 such biphenyl fragments were retrieved from the Cambridge Structural Database. The calculated population distribution was derived from the Boltzmann inversion of an experimentally derived torsion potential for an isolated molecule; this potential has an energy minimum at a twist angle of 44° and small barriers at twist angles of 0° and 90°. Comparison of the observed and calculated distribution functions shows that nearly planar biphenyl fragments are found to occur much more often than expected. Nearly planar conformations, which lie ca. 6 kJ/mol above the minimum of the intramolecular potential energy surface, appear to be favored systematically in the solid state; contrary to the usual assumption of the structure correlation method, the effects of crystal packing on the molecular conformations of these fragments seem not to be completely random. Structures with twist angles below 12° were examined carefully; if possible, the atomic "thermal" parameters were analyzed in terms of the rigid-body model. Evidence of disorder was found for only one of these structures. Librational/torsional motion about the long axis of the biphenyl fragment is inversely correlated with twist angle: the more planar the molecule, the greater the motion. Increased motion raises the mean instantaneous distance between the ortho H atoms and thereby lowers the energy cost of a conformation that is planar on the average.

Comparisons of data from large numbers of crystal structures are commonly used to determine mean molecular geometries, deduce reaction pathways, and identify transition states.[1-3] These data are often retrieved from the Cambridge Structural Database[2,4] (hereafter, the CSD), a compendium of nearly 70 000 structures of molecular crystals; the general procedure is known as the structure-correlation method.[3] Underlying this method is the assumption that molecular structures concentrate in low-energy regions of conformational space in the solid state as they do in the gas phase.[3] But is this assumption always valid? Is it possible for the solid state to systematically favor a molecular conformation that does not correspond to an intramolecular energy minimum?

Conformations that do not correspond to an intramolecular energy minimum are observed from time to time in the solid state; their occurrence is attributed to crystal-packing effects. The structure-correlation method assumes that molecular deformations resulting from packing forces are small in terms of energy and that they are distributed randomly over the normal coordinates. The environment in any individual molecular crystal is almost always anisotropic, but if a structural fragment is observed in a large number of different environments, any directional effects are supposed to be averaged out. Effects of the generally greater density in the solid state, as compared with less condensed phases, are rarely considered. Taken together, these assumptions are

---

(1) Wilson, S. R.; Huffman, J. C. *J. Org. Chem.* **1980**, *45*, 560–566.

(2) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

(3) Bürgi, H.-B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153–161.

(4) 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.* **1979**, *B35*, 2331–2339.

0002-7863/89/1511-4586$01.50/0