dividual rates *may* differ widely. Assay of dynamic processes with a single technique of severely limited time scale, especially a resonance probe, tends to limit the experimentalist's purview. Nuclear magnetic resonance studies may define a nonbond-breaking mechanism as the origin of stereochemical lability, but there may be a dissociative process, differing in rate by only 10^2, contributing significantly to the general phenomenon.

Topological delineation of stereoisomeric processes is being developed for 3- through 12-atom aggregates. Solutions are being sought primarily in polytopes and toruses to maximize the possibility of facile progression to a potential energy surface. An initial paper, to be submitted shortly, will outline definitions,[29] constraints, and approaches to generic topological representations.

(29) *E. g.*, isomer numbers, connectivity, closed and open systems, subsystems, subcycles, and enantiomer traverse.

Structural Studies of Pentacoordinate Silicon. II. Phenyl(2,2′,2″-nitrilotriphenoxy)silane[1]

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Abstract: The molecular and crystal structure of $(C_6H_5)Si(OC_6H_4)_3N$ has been determined from three-dimensional X-ray diffraction data. The space group is $Cmc2_1$ with four molecules in an orthorhombic unit cell of dimensions $a = 11.229 \pm 0.003$ Å, $b = 14.767 \pm 0.004$ Å, and $c = 11.940 \pm 0.003$ Å. The molecules exhibit C_s symmetry, with the plane of the phenyl substituent oriented perpendicular to the crystallographic mirror plane. The main features of interest are the Si–N bond length of 2.334 Å, which gives the first direct evidence for Si→N dative bonding in nitrilotriphenoxysilanes, and the C–Si–O bond angles of 100.0° (average), which indicate the geometry at silicon to be distorted slightly further from an ideal trigonal bipyramid than the analogous nitrilotriethoxysilane. Other bond distances at silicon are Si–C = 1.853 Å, Si–O(1) = 1.635 Å, and Si–O(2) = 1.650 Å. The final discrepancy index R_1 is 0.0599 for 858 reflections.

Recent X-ray diffraction studies of dimethylsilylamine pentamer,[2] $(-SiH_3N(CH_3)_2-)_5$, and phenylnitrilotriethoxysilane,[1] $PhSi(OCH_2CH_2)_3N$, have directly established the existence of pentacoordinate silicon in solids. Similar bonding has also been hypothesized to occur in nitrilotriphenoxysilanes,[3] $XSi(OC_6H_4)_3N$. Until the present study, the principal evidence for this assertion was the absence of basicity in these compounds, particularly as compared to certain triarylamines such as azatriptycene, where the rings are constrained from aligning themselves so that their π orbitals can effectively delocalize the N lone-pair electrons. This lack of basicity is consistent with a transannular Si←N dative bond and also occurs in the nitrilotriethoxysilanes.[4] The present single-crystal X-ray diffraction study of phenylnitrilotriphenoxysilane, where X = C_6H_5, provides direct evidence for the existence of this bond and shows that the silicon coordination geometry is even further distorted from an ideal trigonal bipyramid in this structure than in phenylnitrilotriethoxysilane.

Experimental Section

Data Collection. A single crystal, in the shape of a rough sphere of approximately 0.1 mm radius, was examined by photographic methods to determine the space group and preliminary lattice constants, and then carefully centered on a Picker automatic four-circle diffractometer. Accurate lattice constants were obtained by a least-squares refinement of the setting angles of ten reflections with Cu Kα radiation (λ 1.5418 Å). The reciprocal lattice symmetry, D_{2h}, indicated that the crystal belonged to the orthorhombic system, with unit cell dimensions $a = 11.229 \pm 0.003$ Å, $b = 14.767 \pm 0.004$ Å, and $c = 11.940 \pm 0.003$ Å, giving a calculated density $\rho = 1.326$ g cm^{-3} for $Z = 4$. The reflection conditions (hkl, $h + k = 2n$; and $h0l$, $h = 2n$, $l = 2n$) were consistent with space groups $Cmc2_1$, C2cm, and Cmcm. Although Cmcm was considered unreasonable because it required either C_{2h} or C_{2v} molecular symmetry, a final choice between the remaining two space groups could not be made until the structure was determined.

The intensity data were collected using the 2θ scan mode of the diffractometer with Ni-filtered Cu Kα radiation. The X-ray tube was set at a 3° take-off angle, and a detector aperture 4.0 mm square was placed 30 cm from the crystal. Scan angles from 1.9 to 2.5° were employed over the range (0–130°) of 2θ examined. The scan speed was 2°/min. Background counts of 15 sec were taken at each end of the scan by the stationary-crystal–stationary-counter technique. A data set comprising 891 of the 1249 possible reflections in the Cu Kα sphere was observed. The intensities of 28 of these reflections were, however, judged to be too weak to be statistically significant and were omitted from the structure analysis. For the remainder, an error $\sigma(I) = [(0.05I)^2 + N_0 + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_0 - kN_b$ in order to establish the weights $w = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement. Here N_0 is the gross count, N_b is the background count, and k is the ratio of scan time to background time. The data were then corrected for Lorentz and polarization effects and an absolute scale factor and over-all temperature factor were computed by Wilson's method. No absorption corrections were made in view of the low linear absorption coefficient, μ(Cu Kα) = 12.1 cm^{-1}, and the relatively small crystal size.

Structure Determination and Refinement. A three-dimensional sharpened Patterson function was computed.[5a] While the Patter-

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(3) C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *ibid.*, **88**, 2727 (1966).

(4) C. L. Frye, G. E. Vogel, and J. A. Hall, *ibid.*, **83**, 996 (1961).

Table I. Final Atomic Parameters[a]

	Atomic coordinates		
Atom	x	y	z
Si	. . .	0.32430 (8)	. . .
O(1)	0.12352 (25)	0.37903 (19)	−0.02583 (30)
O(2)	. . .	0.25290 (28)	0.10630 (39)
N	. . .	0.42602 (28)	0.15074 (43)
C(1)	0.16893 (36)	0.44891 (26)	0.03551 (39)
C(2)	0.10785 (36)	0.47666 (23)	0.12925 (37)
C(3)	0.15140 (47)	0.55001 (32)	0.19281 (50)
C(4)	0.25238 (51)	0.59435 (31)	0.16067 (61)
C(5)	0.31381 (43)	0.56440 (33)	0.06436 (58)
C(6)	0.27495 (34)	0.49280 (33)	0.00097 (53)
C(7)	. . .	0.27702 (37)	0.21857 (52)
C(8)	. . .	0.36659 (36)	0.24567 (54)
C(9)	. . .	0.39312 (48)	0.35784 (73)
C(10)	. . .	0.32936 (47)	0.44256 (76)
C(11)	. . .	0.23568 (51)	0.40988 (70)
C(12)	. . .	0.20909 (40)	0.29966 (57)
C(13)	. . .	0.24290 (36)	−0.11809 (54)
C(14)	0.10788 (50)	0.21137 (34)	−0.16491 (52)
C(15)	0.10781 (67)	0.14358 (43)	−0.24844 (63)
C(16)	. . .	0.11098 (57)	−0.28806 (83)

		Anisotropic Thermal Displacements (Å)[b]			
$U_{11}^{1/2}$	$U_{22}^{1/2}$	$U_{33}^{1/2}$	$U_{12}^{1/2}$	$U_{13}^{1/2}$	$U_{23}^{1/2}$
0.229 (27)	0.189 (25)	0.170 (28)	. . .	. . .	0.018 (24)
0.249 (40)	0.238 (39)	0.204 (45)	−0.112 (35)	0.105 (35)	−0.088 (36)
0.301 (56)	0.180 (43)	0.183 (51)	. . .	. . .	−0.016 (39)
0.245 (48)	0.189 (44)	0.165 (49)	. . .	. . .	−0.065 (45)
0.241 (45)	0.211 (44)	0.194 (48)	−0.080 (40)	−0.046 (42)	0.079 (39)
0.241 (45)	0.196 (43)	0.199 (51)	0.031 (38)	−0.058 (42)	−0.038 (40)
0.277 (55)	0.228 (48)	0.242 (56)	−0.100 (46)	−0.134 (50)	−0.109 (45)
0.293 (56)	0.240 (48)	0.291 (65)	−0.126 (51)	−0.117 (56)	−0.116 (53)
0.242 (49)	0.268 (53)	0.296 (65)	−0.135 (47)	−0.080 (52)	0.152 (55)
0.239 (44)	0.257 (46)	0.234 (50)	−0.121 (43)	0.033 (49)	0.081 (51)
0.218 (50)	0.204 (50)	0.174 (57)	. . .	. . .	−0.024 (47)
0.251 (55)	0.201 (50)	0.174 (58)	. . .	. . .	−0.028 (48)
0.341 (76)	0.239 (60)	0.196 (65)	. . .	. . .	−0.076 (54)
0.368 (86)	0.253 (62)	0.191 (67)	. . .	. . .	0.060 (57)
0.310 (71)	0.266 (63)	0.204 (70)	. . .	. . .	0.075 (57)
0.271 (61)	0.222 (55)	0.183 (61)	. . .	. . .	0.114 (52)
0.255 (58)	0.191 (51)	0.177 (59)	. . .	. . .	−0.018 (47)
0.284 (56)	0.269 (54)	0.233 (61)	0.123 (49)	0.065 (49)	−0.139 (51)
0.360 (72)	0.279 (57)	0.270 (69)	0.150 (59)	0.129 (64)	−0.168 (60)
0.347 (81)	0.281 (72)	0.240 (72)	. . .	. . .	−0.185 (66)

[a] Numbers in parentheses are estimated standard deviations from the least-squares refinement, $\times 10^5$ for atomic coordinates and $\times 10^3$ for thermal parameters. [b] These values are the square roots of the mean-square amplitude tensors, U_{ij}, based on the expression $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ and the relation, *e.g.*, $\beta_{12} = 2\pi^2 U_{12}a^*b^*$.

son exhibited a concentration of vectors in the 0, y, z plane (a Harker section for C2cm), a detailed analysis of the map revealed that these peaks actually resulted from the atoms in the mirror plane at $x = 0$ of the correct space group Cmc2$_1$. Our initial analysis of the Patterson interactions revealed all of the Si, O, N, and C atoms, although there appeared to be some ambiguity in the positions of the *ortho* and *meta* carbons of the phenyl substituent. Therefore, the final location of these atoms was deferred until the calculation of an electron density function[5a] based on the phases from the other 18 unique atoms. This map clearly indicated that these atoms were located in positions orienting the plane of the phenyl ring perpendicular to the crystallographic mirror plane.

The positional parameters and isotropic temperature factors of all 20 atoms were allowed to vary[5b,6a] in four cycles of full-matrix least-squares refinement. The reliability indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = \{\Sigma w[F_o - F_c]^2/\Sigma wF_o^2\}^{1/2}$ decreased from 0.25 to 0.14 and from 0.41 to 0.22, respectively. At this point, a survey of the data set showed five reflections, (0.0.12) (7.3.3), (0.4.12), (4.6.2), and (0.8.5), with very low observed intensities and large (>25) values of $\Delta F/\sigma$, and these were withdrawn from the refinement. At the same time, a correction for anomalous scattering from silicon was introduced.[6b] Two more cycles of isotropic refinement reduced the discrepancy indices to $R_1 = 0.116$ and $R_2 = 0.166$. Finally, five cycles of refinement[6b] assuming anisotropic thermal motion yielded $R_1 = 0.0599$ and $R_2 = 0.0809$. In the final cycle, the average x, y, z parameter shift was 0.06σ for atoms in general positions and 0.04σ for atoms in the mirror plane. A difference map calculated after the final cycle of isotropic refinement failed to reveal any hydrogen atoms, and therefore these have not been included in the structure factor calculations. Refinement of the structure with data indexed as $\overline{hkl}$ yielded $R_1 = 0.0624$ and $R_2 = 0.0834$. By applying Hamilton's test[7] to the R_2 ratio, $\mathcal{R} = 0.0834/0.0809 = 1.039$, and, noting that

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(5) (a) Fourier calculations were performed on the IBM 7094 using the program ERFR-2 of Shoemaker, Sly, and Van den Hende. (b) Least-squares refinements were carried out on the CDC 3800 using program ANL-FLS14E, J. Gvildys' version of Busing, Martin, and Levy's OR-FLS. (c) ANL-FFE is J. Gvildys' version of OR-FFE, a FORTRAN crystallographic function and error program by Busing, Martin, and Levy. (d) OR-TEP is a FORTRAN thermal-ellipsoid plot program for crystal structure illustrations by C. K. Johnson, Oak Ridge, National Laboratory, Report ORNL 3794, Oak Ridge, Tenn., June 1965. (e) J. Gvildys, Argonne National Laboratory Program Library B-125, 1965; see V. Schomaker, J. Wasser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, **12**, 600 (1959). (f) A few low-order, high-intensity reflections, such as the 020, 200, 110, 220, 111, and 022, were included in the refinement, although they showed a moderate (10–20%) amount of extinction.

(6) (a) Atomic scattering factors were taken from "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–209. (b) Dispersion corrections to the Si scattering factor were taken from the same reference, p 214.

(7) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

Table II. Bond Distances (Å) and Angles (Deg)[a]

Distances	
Si′-N′	2.344 (5)
Si′-O(1)	1.635 (3)
Si′-O(2)′	1.650 (4)
Si′-C(13)′	1.853 (6)
O(1)-C(1)	1.364 (5)
N′-C(2)	1.446 (4)
O(2)′-C(7)′	1.387 (8)
N′-C(8)′	1.434 (7)
C(1)-C(2)	1.375 (6)
C(2)-C(3)	1.410 (6)
C(3)-C(4)	1.364 (8)
C(4)-C(5)	1.412 (9)
C(5)-C(6)	1.372 (8)
C(6)-C(1)	1.417 (6)
C(7)′-C(8)′	1.362 (8)
C(8)′-C(9)′	1.395 (11)
C(9)′-C(10)′	1.382 (11)
C(10)′-C(11)′	1.437 (11)
C(11)′-C(12)′	1.373 (10)
C(12)′-C(7)′	1.394 (8)
C(13)′-C(14)	1.413 (6)
C(14)-C(15)	1.413 (8)
C(15)-C(16)′	1.386 (8)

Angles with the N-Si-C Axis	
C(13)′-Si′-O(1)	100.21 (14)
C(13)′-Si′-O(2)′	99.84 (21)
O(1)-Si′-N′	80.10 (12)
O(2)′-Si′-N′	79.56 (18)
Si′-N′-C(2)	101.25 (25)
Si′-N′-C(8)′	102.41 (30)

Angles about the N-Si-C Axis	
O(1)-Si′-O(2)′	117.46 (13)
O(1)-Si′-O(1m)	116.09 (22)
C(2)-N′-C(8)′	117.18 (26)
C(2)-N′-C(2m)	113.72 (40)

Angles in the Phenyl Ring	
C(13)′-C(14)-C(15)	120.80 (50)
C(14)-C(15)-C(16)′	119.17 (55)
C(15)-C(16)′-C(15m)	121.72 (69)
C(14)-C(13)′-C(14m)	118.03 (60)
C(13)-Si-N	179.40 (22)

Angles in Phenoxy Rings	
C(1)-C(2)-C(3)	119.61 (42)
C(2)-C(3)-C(4)	120.36 (53)
C(3)-C(4)-C(5)	118.99 (47)
C(4)-C(5)-C(6)	122.37 (43)
C(5)-C(6)-C(1)	117.34 (51)
C(6)-C(1)-C(2)	121.31 (42)
C(7)′-C(8)′-C(9)′	120.05 (62)
C(8)′-C(9)′-C(10)′	120.75 (61)
C(9)′-C(10)′-C(11)′	117.20 (74)
C(10)′-C(11)′-C(12)′	122.36 (75)
C(11)′-C(12)′-C(7)′	117.37 (60)
C(12)′-C(7)′-C(8)′	122.27 (56)

Angles in Five-Membered Rings	
Si′-O(1)-C(1)	126.14 (28)
O(1)-C(1)-C(2)	118.42 (35)
C(1)-C(2)-N′	114.07 (35)
C(2)-N′-Si′	101.25 (25)
N′-Si′-O(1)	80.10 (12)
Si′-O(2)′-C(7)′	125.40 (36)
O(2)′-C(7)′-C(8)′	118.63 (55)
C(7)′-C(8)′-N′	114.00 (53)
C(8)′-N′-Si′	102.41 (30)
N′-Si-O(2)′	79.56 (18)

[a] Primed atoms occur in the mirror plane. Atoms labeled m are generated by the mirror plane from the indicated numbered atom. Numbers in parentheses are the estimated standard deviations, ×10³, as calculated from the variance-covariance matrix obtained in the final cycle of least squares.

$\mathcal{R}_{1,868,0.01} < 1.028$, we consider that the sense of the imaginary contribution to the anomalous scattering is correct at the 1% significance level.

Atomic parameters and their estimated standard deviations are listed in Table I, while bond distances and angles[5c] are given in Table II. A table of observed and calculated structure factors has been deposited[8] with the U. S. Library of Congress.

Results and Discussion

The molecular structure of phenyl(2,2′,2′′-nitrilotriphenoxy)silane is shown in Figure 1.[5d] The geometry at the silicon atom can be described as a distorted trigonal bipyramid, in which the three equatorial oxygen atoms are bent away from the phenyl substituent toward the nitrogen atom. The average C-Si-O angle is 100.0°, somewhat larger than the value of 97.3° observed for the triethoxy analog[1] and approximately halfway between the 90° of an ideal trigonal bipyramid and the tetrahedral angle of 109.5°. However, the O(2)-Si-O(1) angle of 117.5° and the O(1)-Si-O(1m) angle of 116.1° are not greatly different from the 120° of the ideal trigonal bipyramid. Atoms N, Si, and C(13) are collinear within experimental error: the average deviation from a least-squares line[5e] ($y = 0.331 + 0.044t$, $z = 0.011 + 0.064t$) through these atoms is 0.005 Å.

The observed Si-N bond distance, 2.344 ± 0.005 Å, is even longer than the value (2.179 Å) observed in phenylnitrilotriethoxysilane[1] and is about 0.5 Å longer than a normal Si-N single bond. These molecular parameters indicate that the strength of the Si←N interaction (believed to be a 3d ← 2p π bond) is substantially less in the nitrilotriphenoxysilanes than in the nitrilotriethoxy compounds. Conjugation effects cannot account for this phenomenon, since the π orbitals of the phenyl rings are orthogonal to the N lone-pair orbital and thus cannot delocalize its electrons. However, in other cases where conjugation effects are negligible, inductive effects have been shown to reduce the basicities of arylamines with respect to their aliphatic analogs.[9] Such an effect in this case must work in the

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[8] This table has been deposited as Document No. 9981 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[9] B. M. Wepster, *Rec. Trav. Chim.*, 71, 1159, 1171 (1952).

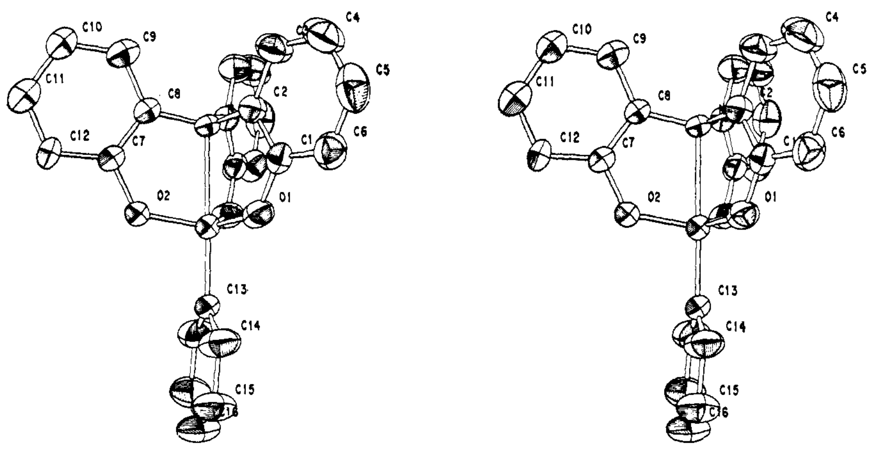

Figure 1. Three-dimensional view of the molecular structure of phenyl(2,2',2''-nitrilotriphenoxy)silane, showing ellipsoids of thermal motion.

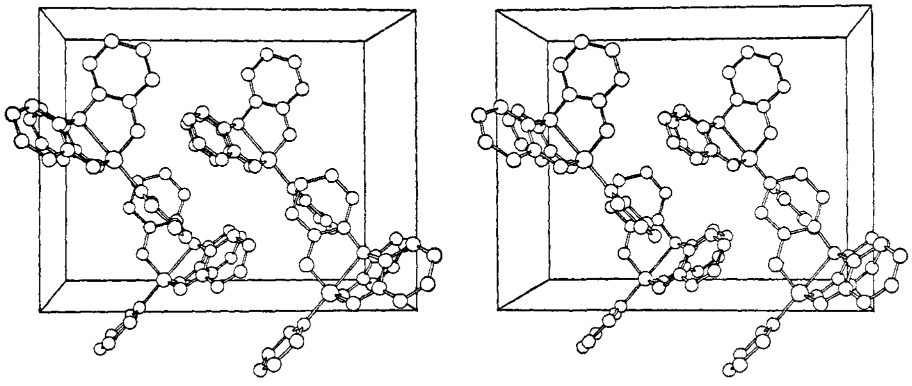

Figure 2. Three-dimensional diagram of the molecular packing in a unit cell of phenyl(2,2',2''-nitrilotrilotriphenoxy)silane. The view is down the x axis, with z vertical.

direction of weakening the Si→N bond. Steric forces must also play an important role in limiting this interaction, since the five-membered rings of nitrilotriphenoxysilanes are planar and do not allow as close an approach of N to Si as in the nitrilotriethoxysilanes, where the rings can pucker to a decidedly nonplanar conformation.[1] The presence of these steric forces can be seen in the bond angles of the phenoxy bridges. For example, the angles at C(1), C(2), C(7), and C(8) are reduced from the 120° value characteristic of sp^2 hybridization, with maximum strain occurring at C(2) and C(8), where the internal angles are 114.1 and 114.0°, respectively. Additional strain arises from the distortion of the tetrahedral geometry at nitrogen, where the C(8)–N–Si and C(2)–N–Si angles are 102.4 and 101.2°, respectively.

The Si–C bond length, 1.853 Å, falls between the value 1.843 Å reported in phenylsilane[10] and the average Si–C distance of 1.875 Å found in a hexaphenyl-3-azacyclotrisiloxane derivative.[11] The Si–O bonds (1.635 and 1.650 Å) and the N–C distances (1.434 and 1.446 Å) are normal, as are the distances in the substituent phenyl group. However, bond distances in the phenoxyphenyl rings seem to be alternately short and long. Beginning with the bonds C(1)–C(2) and C(7)–C(8), the average distances around the rings are 1.368, 1.402, 1.373, 1.424, 1.372, and 1.406 Å. This apparent localization of double-bond character may originate in the bond angle distortions discussed previously.

The dihedral angle between the five-membered ring in the mirror plane and either of the others is 121.4°, while that between the two mirror-related rings is 117.2°. This significant distortion from ideal threefold symmetry about the N–Si–C(13) axis may result from the close approach (2.986 Å) between C(14) of the substituent phenyl group and O(1), and likewise between C(14m) and O(1m). This distortion is of course also reflected in the O–Si–O and C–N–C bond angles.

The crystal structure is depicted in Figure 2.[5d] The molecules are packed so that the phenoxy ring in a given mirror plane rests in the angle between the two mirror-related phenoxy rings of a neighboring molecule situated on the same mirror plane. The substituent phenyl ring of another molecule in the same plane approaches this phenoxy ring from the other side and is oriented perpendicular to it. All remaining phenyl rings approach each other at angles as close to 90° as possible. There are no unusually close intermolecular constants.

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(10) F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956).

(11) W. Fink and P. J. Wheatley, *J. Chem. Soc., A*, 1517 (1967).