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John J. Stezowski [a] , Rolf-Dietrich Stigler [a] , Norbert Karl [b] & Klaus Schuller [b]

[a] Institu für Organische Chemie, Biochemie und Isotopenforschung

[b] Physikalisches Institut-Teil 3, Universität Stuttgart, D-7000, Stuttgart, 80

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Characterization of a 1:1 Complex of Unusual Structure in the Binary Phenothiazine:Phenazine System

JOHN J. STEZOWSKI and ROLF-DIETRICH STIGLER
Institut für Organische Chemie, Biochemie und Isotopenforschung

and

NORBERT KARL and KLAUS SCHULLER
Physikalisches Institut-Teil 3, Universität Stuttgart, D-7000 Stuttgart 80

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The phase diagram for the binary system phenothiazine and phenazine has been examined and found to demonstrate the existence of a 1:1 phase. Crystals of this phase are dark red in color and display a visible absorption spectrum which seems indicative of a π-molecular donor:acceptor complex. A crystal structure determination has been carried out; space group $P2_1/c$: a = 9.072(2), b = 8.872(2), c = 25.934(5) Å, β = 112.65(2)°, and Z = 4. The crystal structure reveals interactions between the components that differ markedly from those commonly observed for weak π-molecular donor:acceptor complexes. Instead of the infinite stacks of alternating donor and acceptor molecules, the phenothiazine and phenazine molecules are nearly mutually perpendicular. There is an intermolecular hydrogen bond in which the phenothiazine molecule serves as the donor. A center of inversion gives rise to a "dimer" in which the two phenazine molecules are stacked with their mean planes separated by 3.714 Å. Any induced polarization resulting from the intermolecular hydrogen bonding in the monomer is balanced by symmetry in the dimer. Consequently, the dimer may be appropriately regarded as the crystallographic packing unit.

INTRODUCTION

Phenothiazine, *PTZ*, and phenazine, *Ph*, both display donor properties in π-molecular complexes with suitable acceptors such as pyromellitic dianhydride, *PMDA*. The crystal structures of the 1:1 complexes of *PTZ*:*PMDA*[1] and *Ph*:*PMDA*[2] both display the usual infinite stacks of alternating donor and acceptor molecules (. . . DADA . . . stacks), though they differ in packing symmetry probably as the result of differences in the molecular symmetries of *PTZ* and *Ph*. The latter is planar with *mmm* symmetry, whereas the former is nonplanar with only one molecular mirror symmetry plane. Interestingly, *PTZ* is more nearly planar in the crystalline 1 : 1 complex with *PMDA* than it is in the crystals of uncomplexed *PTZ*. It remains to be determined whether or not the degree of planarity of *PTZ* in π-molecular complexes is purely the result of packing effects or is dependent upon its electronic interactions with acceptors of different electron affinities.

Phase diagram studies for the system of the donor-type *PTZ* and *Ph* molecules have revealed the existence of a phase of composition 1 : 1. The color of the crystalline sample and its visible absorption spectrum were considered to be indicative of a π-molecular donor:acceptor, $D{:}A$, complex. In order to further characterize this phase, we have carried out a crystal structure determination.

EXPERIMENTAL

Phase Diagram and Chemical Analysis

A differential scanning calorimeter (Perkin Elmer, DSC 2) was used to investigate the binary phase diagram of *PTZ* and *Ph*. Calibration of the temperature scale was performed with samples of indium and lead. The beginning and end of the melting intervals were determined by the intersection of the tangents to the raising and decaying branches of the DSC curve with the elongated base line; a slight empirically established correction was applied to the end (liquidus) temperature, taking into account the finite heating rate.

Samples, typically of 2 mg, were taken from either crystals, obtained by slow sublimation in evacuated ampules (plate sublimation[3]), or from bars which were obtained by slow directional solidification ("normal freezing")[4] and hermetically sealed into aluminum pans. The concentrations of the measured samples or of parallel slices were determined by UV absorption spectroscopy on 10^{-4} molar solutions in n-hexane (numerical evaluation of the extinction at several wavelengths between 280 and 370 nm was used). Above 15% *PTZ*, an error span of ±2.5% can be assumed for this method. Below 15% *PTZ* the accuracy of the analysis by absorption spectroscopy was lower because the *PTZ* molar extinction coefficient is smaller than that of *Ph*. In these cases, we also applied isotopic dilution mass spectrometry[5] adding known fractions of perdeuterated phenazine for this purpose. The concentrations of several samples were further checked by gas chromatography of benzene solutions on 2 meter XE-60 columns.

X-ray Crystallography

Dark red crystals of the 1:1 *PTZ*:*Ph* phase were grown by high vacuum plate sublimation techniques[3]. All X-ray diffraction measurements were made at room temperature (24(1)°C) with a triangular-prismatic crystal ($0.25 \times 0.28 \times 0.35$ mm^3) sealed in a thin-walled glass capillary.

The Laue symmetry and systematic extinctions correspond to space-group $P2_1/c$ with lattice parameters: $a = 9.072(2)$, $b = 8.872(2)$, $c = 25.934(5)$ Å and $\beta = 112.65(2)°$; Z = 4, and the chemical formula $C_{12}H_9NS:C_{12}H_8N_2$ give $\rho_{calc} = 1.307$ g cm^{-3}. The lattice parameters were obtained by least-squares refinement[6] with the 2θ values of 20 automatically centered reflections in the angular range $30.3 < 2\theta < 35.78°$ (monochromatized MoK$_\alpha$ radiation).

Diffraction intensities were measured to a resolution $(\sin \theta/\lambda)_{max} = 0.65$ Å^{-1} with a Syntex $P\bar{1}$ autodiffractometer operating in an ω-scan mode for which the scan range was 0.75°, and the scan rate varied from 2.0 to 24.0° min^{-1} as a function of maximum reflection intensity; background intensity was measured on each side of a reflection ($\Delta\omega = 1.0°$) for one-half the total scan time. Three reference reflections, measured periodically, remained constant to within 1.5% of their initial intensities. Of the 4421 unique reflections measured, 2652 were classified as "observed" under the criterion $I > 2\sigma(I)$. Data were corrected for Lorentz and polarization effects but not for absorption, $\mu = 1.8$ cm^{-1}.

Structure Determination and Refinement

The initial structural model was determined by direct methods and developed by least-squares refinement and difference Fourier techniques; all hydrogen atoms were located in difference electron density maps. Atomic coordinates for all atoms, anisotropic temperature factors for *C*, *N*, and *S* atoms, isotropic temperature factors for H-atoms, and a single scale factor were refined. Dispersion effects for *S* were included in the structure factor calculations. A total of 3156 reflections (all observed reflections and those "unobserved" reflections for which the calculated structure factor was greater than the arbitrary cut off value) contributed to the refinement of 321 parameters to give $R = 0.051$ and $R_w = 0.066$, where $w = \{\sigma(F) + 0.025|F_0| + 0.0001|F_0|^2 + 0.00001|F_0|^3\}^{-1}$; the estimated standard deviation of an observation of unit weight was 1.43.

RESULTS AND DISCUSSION

Phase Diagram

The phase diagram, Figure 1, clearly indicates the existence of a 1 : 1 phase, melting at 435.9(3) K, in the binary *PTZ* : *Ph* system. Phenazine and the 1 : 1 phase, as well as the 1 : 1 phase and phenothiazine, form simple eutectic binary phase diagrams without miscibility. A minute range of miscibility at the *Ph*-rich terminal end of the phase diagram cannot be excluded since sublimation ampoules containing an excess of phenazine displayed orange crystals in addition to the dark red crystals of the 1 : 1 phase; pure phenazine is light yellow. The *Ph*-rich eutectic, melting at 427.4(6) K, appears at 26.7 mol% *PTZ*, the *PTZ*-rich eutectic at 65.0 mol% *PTZ* and melts at 431.6(4) K. Eutectic compositions of 25.5 and 66.3 mol% *PTZ* result from a plot of the eutectic enthalpies of melting *vs* composition and numerical curve fitting by linear regression (known as Tammann's triangle method); these values are in fair agreement with the above values.

As indicated earlier, the *PTZ* molecule is normally bent along its *N*-*S* axis, whereas the *Ph* molecule is planar. Consequently, a considerable range of miscibility was not expected. The dark red color (due to a broad unstructured absorption edge from 660 to 580 nm) of the molecular 1 : 1 complex between the two light yellow-colored components suggested some

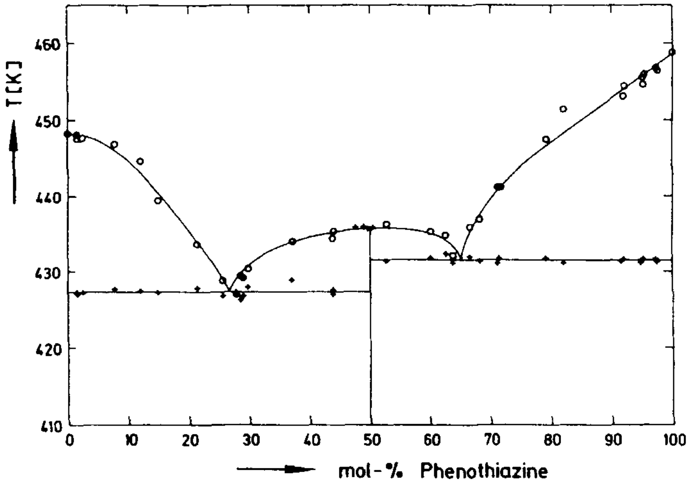


FIGURE 1 The phase diagram for phenothiazine/phenazine obtained by application of differential scanning calorimetry techniques.

TABLE I

Fractional atomic coordinates with estimated standard deviations.

Atom	*X*	*Y*	*Z*
C(1)	.5788(3)	.2290(3)	.3962(1)
C(2)	.4399(4)	.2151(3)	.4049(1)
C(3)	.3150(4)	.1335(4)	.3685(1)
C(4)	.3318(3)	.0614(3)	.3240(1)
C(5)	.4741(3)	.0683(2)	.31612(9)
S(6)	.49883(8)	−.04377(7)	.26363(3)
C(7)	.6561(3)	.0524(2)	.25376(9)
C(12)	.7625(2)	.1428(2)	.29555(9)
N(13)	.7443(2)	.1628(2)	.34620(8)
C(14)	.5993(2)	.1544(2)	.35236(8)
C(8)	.6778(4)	.0306(4)	.2047(1)
C(9)	.8056(5)	.0959(5)	.1970(1)
C(10)	.9114(4)	.1851(4)	.2383(1)
C(11)	.8876(3)	.2099(3)	.2868(1)
C(15)	.8699(4)	.2317(3)	.5730(1)
C(16)	.9972(5)	.1764(4)	.6139(2)
C(17)	1.1312(5)	.2669(5)	.6420(2)
C(18)	1.1357(3)	.4134(4)	.6278(1)
C(19)	1.0016(3)	.4773(3)	.58389(9)
N(20)	1.0044(2)	.6227(2)	.57034(7)
C(21)	.8748(3)	.6770(3)	.52859(9)
C(26)	.7411(2)	.5826(3)	.50009(8)
N(27)	.7377(2)	.4384(2)	.51427(8)
C(28)	.8667(3)	.3851(2)	.55559(9)
C(22)	.8711(4)	.8288(3)	.5122(1)
C(23)	.7429(6)	.8833(5)	.4702(2)
C(24)	.6105(5)	.7925(5)	.4419(1)
C(25)	.6078(3)	.6462(4)	.4559(1)
H(1)	.665(3)	.289(2)	.4200(9)
H(2)	.423(3)	.268(3)	.435(1)
H(3)	.216(4)	.131(3)	.371(1)
H(4)	.251(3)	.004(3)	.299(1)
H(13)	.807(3)	.216(3)	.367(1)
H(8)	.604(3)	−.036(3)	.175(1)
H(9)	.823(4)	.075(3)	.165(1)
H(10)	1.000(3)	.231(3)	.236(1)
H(11)	.956(3)	.270(3)	.317(1)
H(15)	.782(4)	.177(3)	.551(1)
H(16)	.995(3)	.075(4)	.627(1)
H(17)	1.222(4)	.228(4)	.667(1)
H(18)	1.221(3)	.480(3)	.645(1)
H(22)	.973(4)	.891(4)	.533(1)
H(23)	.730(5)	.980(4)	.462(2)
H(24)	.530(4)	.836(4)	.414(1)
H(25)	.524(3)	.583(3)	.441(1)

sort of charge transfer, *CT*, interaction between a donor and acceptor molecule. In view of these optical properties the results of the crystal structure determination are surprising.

Crystal Structure

Fractional atomic coordinates are presented in Table I and thermal parameters are contained in Table II. Selected bond distances and bond angles are depicted in Figure 2; crystal packing is illustrated in stereoscopic projection[7] in Figure 3.

The molecular conformation of the components is observable in Figures 3a and 3b. The *Ph* molecule displays a close approximation to planarity, Table III, and nearly ideal *mmm*-symmetry in its bonding geometry. The *PTZ* molecule displays a bent conformation, illustrated in Figure 3b, in which the angle between the mean planes fit to the aromatic rings is 159.7°. This *PTZ* conformation is very similar to that reported for uncomplexed *PTZ* in three crystal modifications[8-10] where the relevant angles are 153.3 and 158.5°. The bonding geometry of the *PTZ* molecule displays a good approximation to mirror symmetry.

TABLE IIa

Anisotropic temperature factors

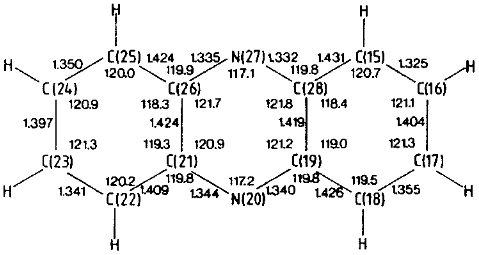
$e^{-2\pi^2}(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + hkU_{12}a^*b^* + hlU_{13}a^*c^* + klU_{23}b^*c^*)$

Atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
C(1)	.067(2)	.064(1)	.054(1)	−.002(1)	.016(1)	.002(1)
C(2)	.085(2)	.081(2)	.072(2)	.007(2)	.031(2)	.008(1)
C(3)	.068(2)	.105(2)	.098(2)	.000(2)	.034(2)	.010(2)
C(4)	.057(1)	.081(2)	.084(2)	−.011(1)	.008(1)	.006(2)
C(5)	.052(1)	.057(1)	.056(1)	−.002(1)	.002(1)	.005(1)
S(6)	.0715(4)	.0694(4)	.0716(4)	−.0147(3)	.0031(3)	−.0196(3)
C(7)	.066(1)	.060(1)	.051(1)	.011(1)	.005(1)	−.003(1)
C(12)	.051(1)	.055(1)	.051(1)	.009(1)	.005(1)	.001(1)
N(13)	.051(1)	.073(1)	.050(1)	−.013(1)	.0045(9)	−.014(1)
C(14)	.050(1)	.051(1)	.047(1)	−.001(1)	.0037(9)	.0064(9)
C(8)	.098(2)	.092(2)	.065(2)	.002(2)	.019(2)	−.018(2)
C(9)	.130(3)	.131(3)	.072(2)	.008(3)	.050(2)	−.010(2)
C(10)	.087(2)	.111(2)	.094(2)	.007(2)	.044(2)	.008(2)
C(11)	.061(1)	.082(2)	.064(2)	.003(1)	.018(1)	−.002(1)
C(15)	.097(2)	.057(2)	.111(2)	−.004(2)	.036(2)	−.006(2)
C(16)	.118(3)	.071(2)	.142(3)	.021(2)	.047(3)	.022(2)
C(17)	.095(3)	.111(3)	.107(3)	.046(2)	.029(2)	.033(2)
C(18)	.062(2)	.098(2)	.079(2)	.007(2)	.011(1)	.009(2)
C(19)	.054(1)	.067(1)	.051(1)	.000(1)	.020(1)	−.001(1)
N(20)	.058(1)	.067(1)	.054(1)	−.016(1)	.0139(9)	−.0029(9)
C(21)	.063(1)	.064(1)	.049(1)	−.009(1)	.022(1)	.000(1)
C(26)	.054(1)	.070(1)	.044(1)	−.002(1)	.017(1)	−.003(1)
N(27)	.061(1)	.065(1)	.061(1)	−.012(1)	.016(1)	−.013(1)
C(28)	.063(1)	.057(1)	.060(1)	−.004(1)	.024(1)	−.009(1)
C(22)	.107(2)	.073(2)	.083(2)	−.019(2)	.026(2)	.013(2)
C(23)	.138(3)	.090(3)	.105(3)	.009(2)	.030(2)	.042(2)
C(24)	.100(3)	.128(3)	.078(2)	.030(2)	.023(2)	.041(2)
C(25)	.064(2)	.113(3)	.060(2)	−.002(2)	.011(1)	.007(2)

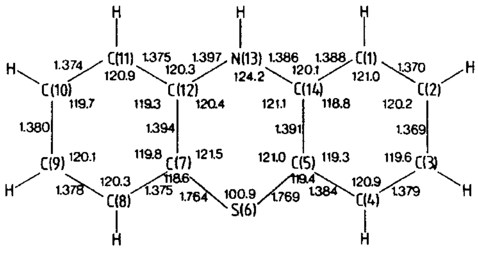
TABLE IIb

Isotropic temperature factors

Atom	*U*
H(1)	.065(7)
H(2)	.092(9)
H(3)	.11(1)
H(4)	.083(8)
H(13)	.066(8)
H(8)	.10(1)
H(9)	.12(1)
H(10)	.10(1)
H(11)	.077(7)
H(15)	.10(1)
H(16)	.11(1)
H(17)	.11(1)
H(18)	.078(8)
H(22)	.14(1)
H(23)	.16(2)
H(24)	.13(1)
H(25)	.091(9)



Ph



PTZ

FIGURE 2 Selected bond distances and bond angles for phenothiazine and phenazine in the 1:1 complex. The estimated standard deviations in the bond distances and angles presented are less than 0.006 Å and 0.4°, respectively. The atom labeling scheme is also presented.

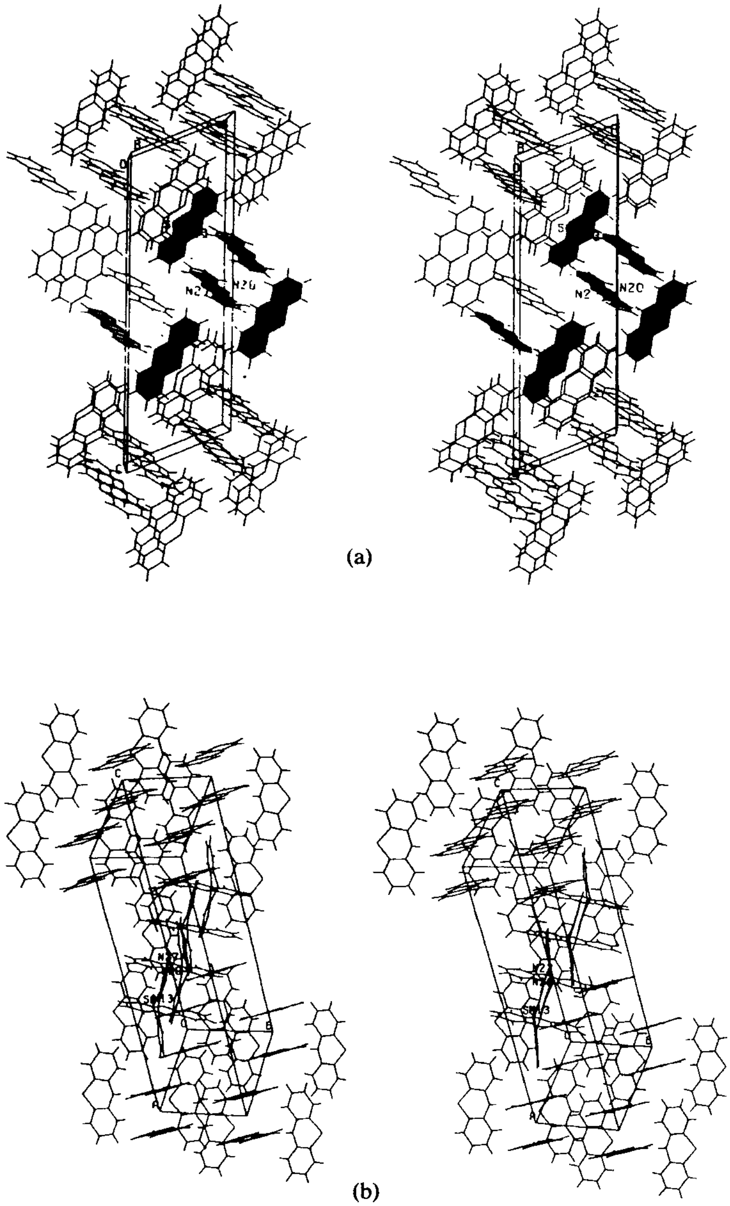


FIGURE 3 Two stereoscopic packing diagrams. The upper figure, 3a, contains two shaded regions; the left region emphasizes the contents of an asymmetric unit and illustrates the hydrogen bonding interaction between phenothiazine and phenazine. The shaded region on the right illustrates the "dimer" of the *PTZ*:*Ph* complex and the two stacked Ph molecules. The lower figure, 3b, illustrates the conformation of *PTZ* in a view nearly down the *N*. . . *S* axis. Crystallographic axes are labeled in the projections.

TABLE III

Least-squares mean planes*

The *i*, *j*, and *k* axes of the orthogonal coordinate system are in the directions *a*, *b*, and $a \times b$ respectively. In that coordinate system:

Plane 1: the *Ph* molecule
$-0.7056i + 0.2626j + 0.6581k = 1.857$ Å
$\sigma = 0.009$ Å
Plane 2a: One aromatic ring of *PTZ* (C(7)—C(12))
$0.4435i - 0.8012j + 0.4018k = 3.579$ Å
$\sigma = 0.008$ Å
Plane 2b: The second aromatic ring of *PTZ*
$0.1367i - 0.8078j + 0.5734k = 3.991$ Å
$\sigma = 0.014$ Å
Plane 2c: The *PTZ* molecule
$0.3048i - 0.7986j + 0.5190k = 3.702$ Å
$\sigma = 0.256$ Å

Selected acute interplanar angles
Plane 1/Plane 2*c* = 85.2°
Plane 2*a*/Plane 2*b* = 20.3°

*Hydrogen atom coordinates were not employed in the calculation of mean planes.

The crystal packing differs markedly from that usually observed in 1 : 1 π-molecular *D* : *A* complexes such as *PTZ* : *PMDA*[1] and *Ph* : *PMDA*.[2] In contrast to the usual $\cdots$ DADA $\cdots$ stacks, where the molecules are nearly coplanar, the mean planes fit to the *PTZ* and *Ph* molecules are nearly perpendicular, Table III. Two *Ph* molecules, related by an inversion center, are stacked, Figure 3, such that their mean planes are separated by 3.714 Å. The mean planes, Table III, of the two neighboring *PTZ* molecules, related by a glideplane, display an interplanar angle of 74.0°.

The *PTZ* and *Ph* molecules of the crystallographic asymmetric unit interact *via* a hydrogen bond between the *PTZ N-H* moiety and one nitrogen atom of the *Ph* molecule (the relevant distances and angles are: $N(13)—H(13) = 0.78(2)$, $H(13) \cdots N(20) = 2.34(3)$, $N(13) \cdots N(20) = 3.115(2)$ Å, and $N(13)—H(13) \cdots N(20) = 179(2)°$). This interaction between *PTZ* and *Ph* can be viewed in Figure 3a where an appropriate molecule of each has been emphasized. These hydrogen bonded donor and acceptor molecules may be regarded as a monomer of the molecular complex. Two monomers, related by an inversion center, are apparently associated into a dimer that may then be regarded as the crystallographic packing unit. Any induced dipole in the *Ph* molecule, resulting from the hydrogen bonding, is thus balanced by the second moiety in the

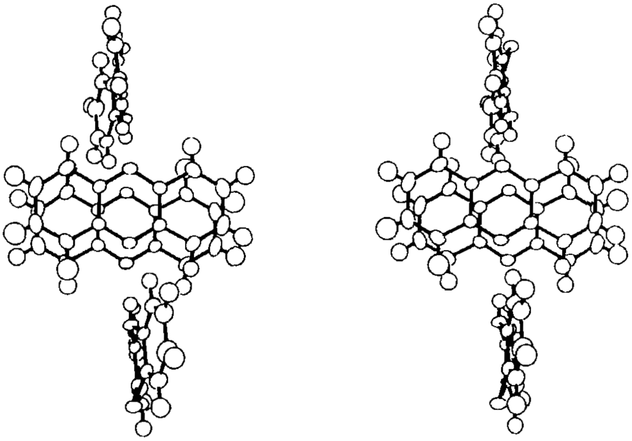


FIGURE 4 A stereoscopic projection of the "dimeric" crystal packing unit viewed along a vector perpendicular to the plane of a *Ph* molecule. The atoms are depicted with thermal ellipsoids consistent with the refined temperature factors.

dimer. An example of this dimer has also been shaded for emphasis in Figure 3a and is presented with thermal ellipsoids in Figure 4.

There is no evidence of hydrogen bonding to the second *Ph* nitrogen atom, *N*(27), or to the *PTZ* sulfur atom; nor does the packing arrangement indicate any π-orbital overlap beyond that between two *Ph* molecules within a dimer. Consequently, crystal packing appears to be stabilized by van der Waals interactions between dimers.

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