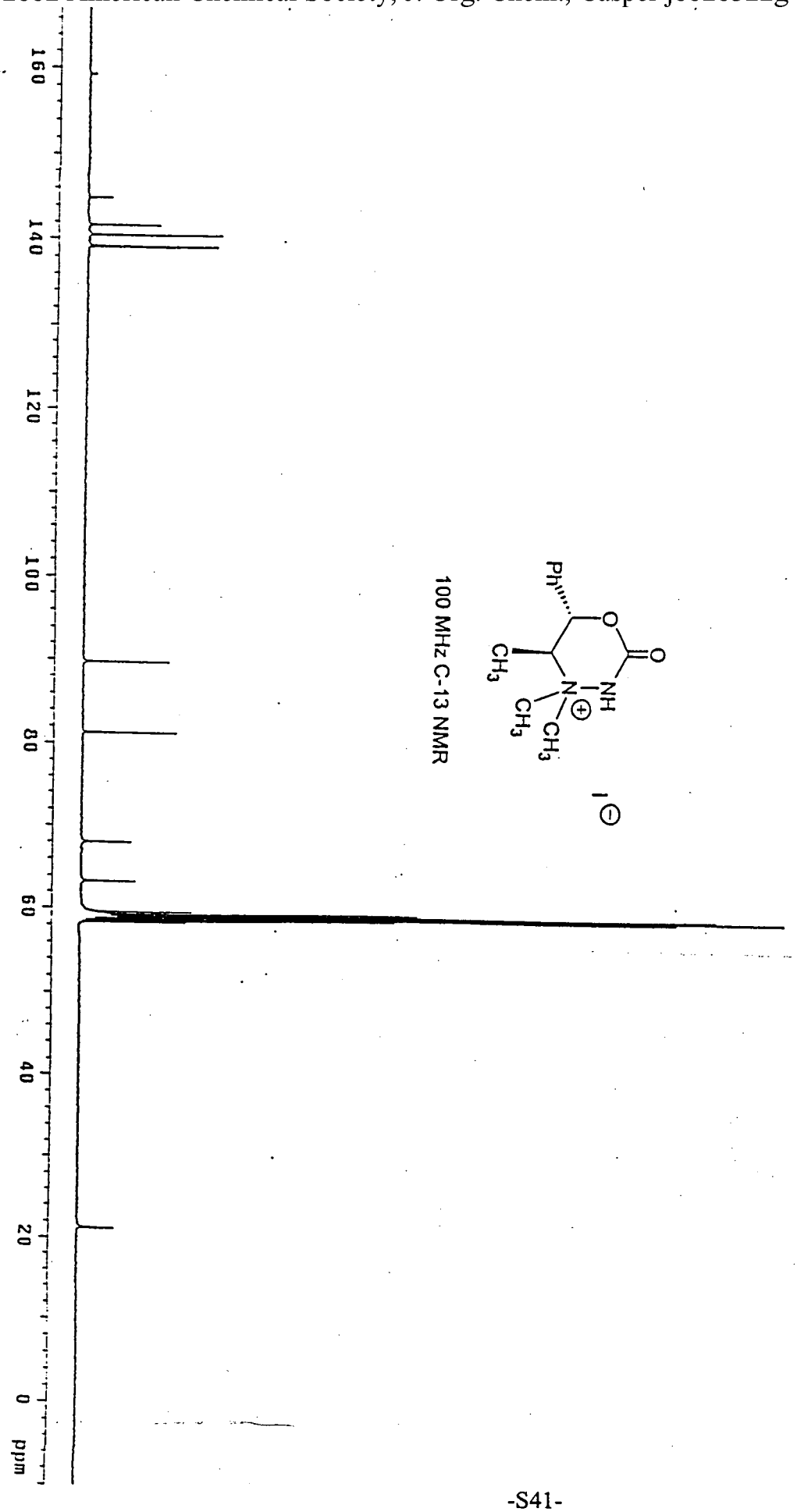
100 MHz ^{13}C NMR of **4a**

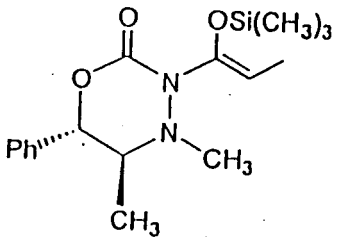


100 MHz C-13 NMR

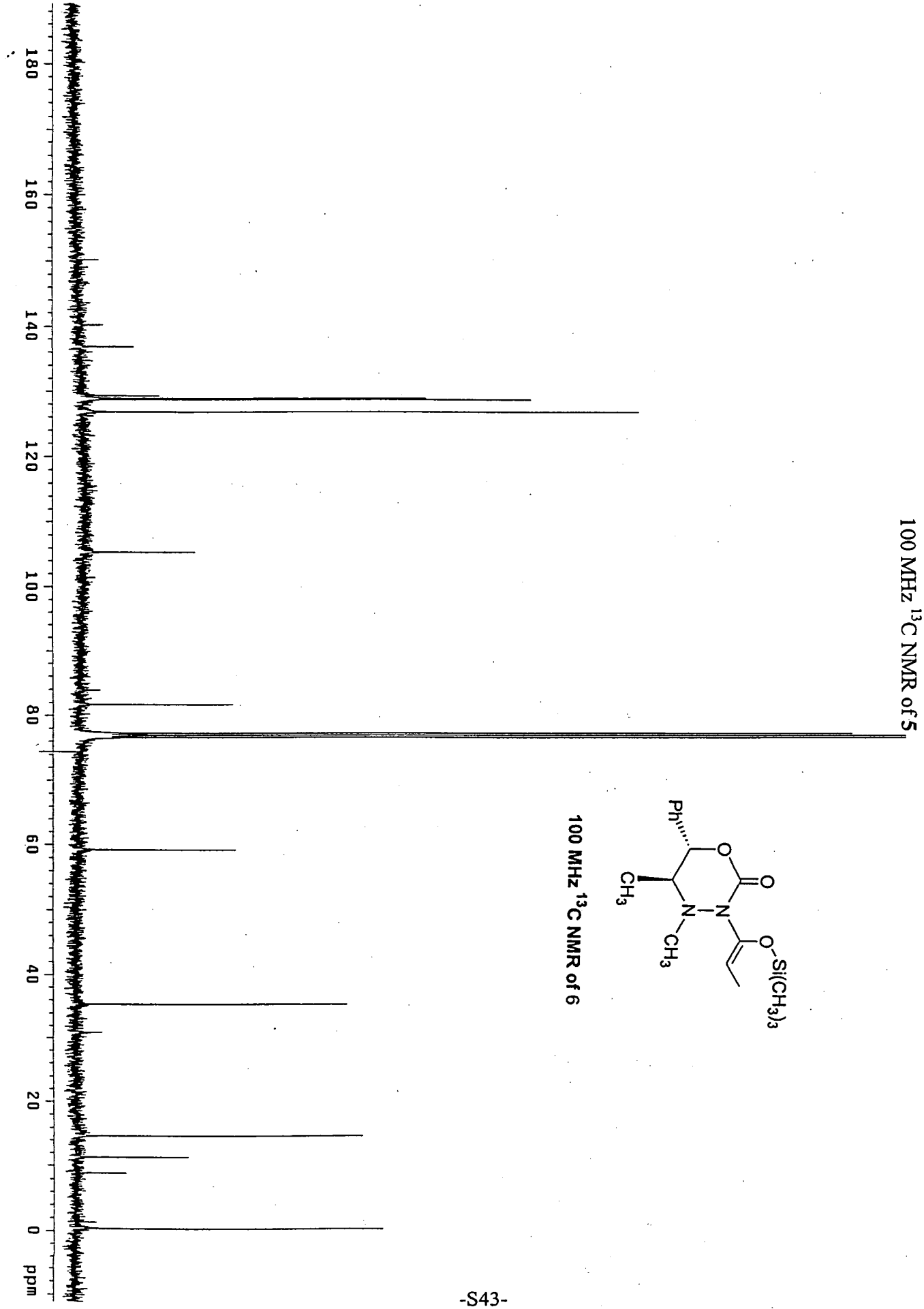
PseudoPropylSilylEnolEther

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "isu400"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 63.0 degrees
Acq. time 1.995 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 400.1488625 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec

400 MHz ^{1}H NMR of 5



400 MHz ^{1}H NMR



100 MHz ^{13}C NMR of **5**

100 MHz ^{13}C NMR of 6

Illinois State University Department of Chemistry

Structure Determination Laboratory

STRUCTURE REPORT

Compounds: (5*S*,6*R*)-3-acetyl -4,5-dimethyl-6-phenyl-2*H*-1,3,4-oxadiazinan-2-one (**2a**)

(5*S*,6*R*)-4,5-dimethyl-6-phenyl-3-propionyl-2*H*-1,3,4-oxadiazin-2-one (**2b**)

Formula: $C_{13}H_{16}N_2O_3$ (**2a**)

$C_{14}H_{18}N_2O_3$ (**2b**)

Crystallographer(s): G. M. Ferrence and Joel. M. Esken

Other Authors of Corresponding Manuscript: David M. Casper, Jennifer R. Blackburn, Christopher D. Maroules, Tana Brady, Jean M. Standard

Crystal Structure Determination of oxadiazinan-2-one 2a. X-ray quality crystals were obtained by recrystallization from a solution of ether and hexanes. A colorless block of approximate dimensions 1.5 x 0.71 x 0.32 mm was mounted on a glass fiber with super-glue and transferred to a Brucker-Nonius CAD4/Mach3 diffractometer. The X-ray diffraction data were collected at room temperature using Mo-K_α radiation. Data collection and cell refinement was performed using CAD4 Express.[1] Data reduction was carried out using XCAD4.[2] The unit cell parameters were obtained from a least-squares refinement of 25 centered reflections. The systematic absences indicated the space group *P 21 21 21* (no. 19).[3] Oxadiazinan-2-one **2a** was found to crystallize in the orthorhombic crystal system with the following unit cell parameters: *a*

= 6.1546(14) Å, b = 9.3877(22) Å, c = 22.5579(54) Å, Z = 4. A total of 2954 reflections were collected, of which 2559 were unique, and 2070 were observed $F^2_o > 2\sigma(F^2_o)$.

Solution and data analysis was performed using the WinGX software package.[4] The structure of **2a** was solved using the direct method program SIR-92[5] and the refinement was completed using the program SHELXL-97.[6] Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms, and were given thermal parameters of 20% greater than those of the attached atoms. Full-matrix least-squares refinement on F^2 led to convergence with R_1 = 0.036 and wR_2 = 0.109 for 2070 data with $F^2_o > 2\sigma(F^2_o)$. A final difference Fourier synthesis showed features in the range of + 0.113 to -0.135 $e^-/Å^3$. An ORTEP drawing of the refined structure **2a** is depicted in Figure 1.[7]

Crystal Structure Determination of oxadiazinan-2-one 2b. X-ray quality crystals of **2b** were obtained by recrystallization from a solution of ether and hexanes. A colorless block of approximate dimensions 0.57 x 0.57 x 0.57 mm was mounted, and the data was collected and analyzed in the same manner as **2b** with the exception that these data were corrected for absorption through the use of empirical psi-scans.[8] The systematic absences indicated the space group *P 21 21 21* (no. 19).[3] Oxadiazinan-2-one **2b** was found to crystallize in the orthorhombic crystal system with the following unit cell parameters: a = 6.2571(3) Å, b = 12.9524(11) Å, c = 16.9737(14) Å, Z = 4. A total of 3016 reflections were collected, of which 2655 were unique, and 2404 were observed $F^2_o > 2\sigma(F^2_o)$. Full-matrix least-squares refinement on F^2 led to convergence with R_1 = 0.032 and wR_2 = 0. 084 for 2404 data with $F^2_o > 2\sigma(F^2_o)$. A final difference Fourier synthesis showed features in the range of + 0.100 to -0.178 $e^-/Å^3$. An ORTEP drawing of the refined structure **2b** is depicted in Figure 1.[7]

List of Tables

Figure Legends

Figure S1. Perspective view of (5*S*,6*R*)-3-acetyl -4,5-dimethyl-6-phenyl-2*H*-1,3,4-oxadiazinan-2-one, **2a**, molecule showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms have been drawn arbitrarily small and are not labeled.

Figure S2. Perspective view of (5*S*,6*R*)-4,5-dimethyl-6-phenyl-3-propionyl-2*H*-1,3,4-oxadiazin-2-one, **2b**, molecule showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms have been drawn arbitrarily small and are not labeled.

Table 1. Crystallographic Data for **2a**.

molecular formula	$C_{13}H_{16}N_2O_3$
fw, g/mol	248.3
crystal dimensions (mm)	0.57 x 0.57 x 0.57
color, shape	colorless block
crystal system	orthorhombic
space group	*P* 21 21 21
unit cell parameters	
a, Å	6.1546(14)
b, Å	9.3877(22)
c, Å	22.5579(54)
V, Å^3	1303.34(05)
Z	4
ρ(calc´d), g cm^{-3}	1.27
μ, cm^{-1}	0.91
diffractometer	Enraf-Nonius CAD4/Mach3
wavelength, λ, Å	0.71073
temperature, K	298
θ range	1.8 – 26
F(000)	527.9
reflections collected	2954 ($0 \leq h \leq 7, 0 \leq k \leq 11, -27 \leq l \leq 27$)
independent reflections	2559
reflections observed	2070 ($I > 2\sigma_I$)

R indices observed (all data)	0.036 (0.058)
wR2 observed (all data)	0.109 (0.124)
parameters (restraints)	166 (0)
Extinction coefficient	none
Goodness of fit	0.922
Shift/esd max (mean)	0.000 (0.000)
largest difference peak and hole	0.113 and –0.135 e^{-} $Å^{-3}$

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2a**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
O(1)	-0.1274(3)	0.2135(2)	0.3647(1)	0.062*
C(2)	-0.1512(3)	0.2447(2)	0.4225(1)	0.049*
N(3)	-0.1596(2)	0.1301(2)	0.4614(1)	0.046*
N(4)	-0.1574(3)	-0.0113(2)	0.4393(1)	0.052*
C(5)	0.0059(3)	-0.0189(2)	0.3922(1)	0.053*
C(6)	-0.0624(3)	0.0755(2)	0.3411(1)	0.056*
C(7)	0.1088(3)	0.0979(2)	0.2947(1)	0.054*
C(8)	0.2856(4)	0.1849(3)	0.3046(1)	0.064*
C(9)	0.4451(4)	0.1988(3)	0.2623(1)	0.068*
C(10)	0.4300(4)	0.1265(3)	0.2095(1)	0.068*
C(11)	0.2557(5)	0.0408(3)	0.1991(1)	0.070*
C(12)	0.0937(4)	0.0268(2)	0.2410(1)	0.064*
C(13)	0.0479(5)	-0.1699(3)	0.3729(1)	0.080*
C(14)	-0.3789(4)	-0.0562(3)	0.4237(1)	0.072*
C(15)	-0.1565(3)	0.1463(2)	0.5231(1)	0.052*
O(16)	-0.1591(3)	0.2615(2)	0.5461(1)	0.065*
C(17)	-0.1504(5)	0.0120(3)	0.5582(1)	0.072*
O(18)	-0.1637(3)	0.3661(2)	0.4368(1)	0.062*

Fractional atomic coordinates and isotropic displacement parameters (Angstrom squared), with standard deviations in the least significant digits in parentheses. Anisotropically refined atoms are marked with an asterisk (*). The form of the Anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$$

Table 3. Selected Interatomic Distances (Å) for **2a**.

Atom1	Atom2	Distance	Atom1	Atom2	Distance
O(1)	C(2)	1.345(3)	O(1)	C(6)	1.456(3)
C(2)	N(3)	1.388(3)	C(2)	O(18)	1.187(3)
N(3)	N(4)	1.418(2)	N(3)	C(15)	1.400(3)
N(4)	C(5)	1.465(3)	N(4)	C(14)	1.470(3)
C(5)	C(6)	1.512(3)	C(5)	C(13)	1.505(4)
C(6)	C(7)	1.501(3)	C(7)	C(8)	1.379(4)
C(7)	C(12)	1.387(3)	C(8)	C(9)	1.375(4)
C(9)	C(10)	1.374(4)	C(10)	C(11)	1.362(4)
C(11)	C(12)	1.380(4)	C(15)	O(16)	1.200(3)
C(15)	C(17)	1.490(3)			

Table 4. Selected Interatomic Angles (deg) for **2a**.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(2)	O(1)	C(6)	125.2(2)	O(1)	C(2)	N(3)	116.6(2)
O(1)	C(2)	O(18)	118.6(2)	N(3)	C(2)	O(18)	124.8(2)
C(2)	N(3)	N(4)	120.8(1)	C(2)	N(3)	C(15)	122.9(1)
N(4)	N(3)	C(15)	116.8(1)	N(3)	N(4)	C(5)	107.9(1)
N(3)	N(4)	C(14)	110.1(2)	C(5)	N(4)	C(14)	116.7(2)
N(4)	C(5)	C(6)	109.4(2)	N(4)	C(5)	C(13)	112.0(2)
O(1)	C(6)	C(5)	108.7(2)	O(1)	C(6)	C(7)	108.8(2)
C(6)	C(5)	C(13)	112.3(2)	C(5)	C(6)	C(7)	114.7(2)
C(6)	C(7)	C(8)	121.6(2)	C(6)	C(7)	C(12)	119.7(2)
C(8)	C(7)	C(12)	118.6(2)	C(7)	C(8)	C(9)	120.5(2)
C(8)	C(9)	C(10)	120.4(3)	C(9)	C(10)	C(11)	119.7(3)
C(10)	C(11)	C(12)	120.4(3)	C(7)	C(12)	C(11)	120.3(3)
N(3)	C(15)	O(16)	121.8(2)	N(3)	C(15)	C(17)	116.0(2)
O(16)	C(15)	C(17)	122.2(2)				

Table 5. Torsional Angles (deg) for **2a**.

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
O(1)	C(2)	N(3)	C(15)	171.8	O(18)	C(2)	N(3)	C(15)	-8.4
C(2)	N(3)	C(15)	O(16)	4.4	C(2)	N(3)	C(15)	C(17)	-175.7
C(14)	N(4)	C(5)	C(6)	60.0	C(14)	N(4)	C(5)	C(13)	-65.2
N(4)	C(5)	C(6)	C(7)	169.6	C(13)	C(5)	C(6)	C(7)	-65.5
C(5)	C(6)	C(7)	C(12)	104.3	C(6)	C(7)	C(8)	C(9)	177.1
C(6)	C(7)	C(12)	C(11)	-176.1	C(12)	C(7)	C(8)	C(9)	-1.1
C(8)	C(7)	C(12)	C(11)	1.6	C(7)	C(8)	C(9)	C(10)	0.3
C(8)	C(9)	C(10)	C(11)	0.1	C(9)	C(10)	C(11)	C(12)	0.4
C(10)	C(11)	C(12)	C(7)	-1.2	C(5)	C(6)	C(7)	C(8)	-73.9

Table 6. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **2a**.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.075(1)	0.059(1)	0.052(1)	0.025(1)	-0.003(1)	0.002(1)
C(2)	0.0419(9)	0.0504(10)	0.0553(10)	0.0079(9)	-.0001(8)	0.0008(8)
N(3)	0.0428(8)	0.0412(7)	0.0549(8)	0.0018(7)	-.0031(7)	-.0009(6)
N(4)	0.0450(8)	0.0433(8)	0.0686(9)	-.0008(7)	-.0038(8)	-.0027(7)
C(5)	0.047(1)	0.048(1)	0.065(1)	0.007(1)	-0.003(1)	-0.007(1)
C(6)	0.054(1)	0.057(1)	0.057(1)	0.008(1)	-0.008(1)	-0.010(1)
C(7)	0.056(1)	0.055(1)	0.050(1)	0.008(1)	-0.008(1)	-0.007(1)
C(8)	0.071(1)	0.067(1)	0.053(1)	-0.001(1)	-0.010(1)	-0.014(1)
C(9)	0.068(1)	0.072(1)	0.064(1)	-0.009(1)	-0.005(1)	-0.003(1)
C(10)	0.081(1)	0.066(1)	0.059(1)	0.005(1)	0.006(1)	-0.003(1)
C(11)	0.096(2)	0.064(1)	0.050(1)	0.006(1)	0.002(1)	-0.012(1)
C(12)	0.072(1)	0.061(1)	0.060(1)	-0.003(1)	-0.012(1)	-0.012(1)
C(13)	0.087(2)	0.055(1)	0.099(2)	0.013(1)	0.004(1)	-0.012(1)
C(14)	0.054(1)	0.064(1)	0.098(2)	-0.012(1)	-0.005(1)	-0.009(1)
C(15)	0.0402(9)	0.059(11)	0.0571(10)	-.0009(9)	0.0032(8)	0.0009(9)
O(16)	0.0680(9)	0.0667(9)	0.0590(8)	-.0009(8)	0.0063(7)	-.0076(7)
C(17)	0.080(1)	0.070(1)	0.066(1)	-0.005(1)	-0.003(1)	0.014(1)
O(18)	0.0718(9)	0.0467(7)	0.0680(8)	0.0102(7)	0.0048(7)	0.0004(6)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for **2a**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq},Å^2
H(5)	0.14215	0.01920	0.40809	0.064
H(6)	-0.18926	0.03203	0.32209	0.067
H(8)	0.29700	0.23465	0.34011	0.077
H(9)	0.56399	0.25754	0.26952	0.082
H(10)	0.53837	0.13600	0.18110	0.082
H(11)	0.24570	-0.00860	0.16344	0.084
H(12)	-0.02615	-0.03054	0.23311	0.077
H(13A)	0.08755	-0.22627	0.40669	0.096
H(13B)	0.16412	-0.17125	0.34449	0.096
H(13C)	-0.08111	-0.20843	0.35515	0.096
H(14A)	-0.47153	-0.04692	0.45769	0.087
H(14B)	-0.37689	-0.15377	0.41094	0.087
H(14C)	-0.43304	0.00276	0.39218	0.087
H(17A)	-0.13997	0.03451	0.59965	0.087
H(17B)	-0.02652	-0.04352	0.54658	0.087
H(17C)	-0.28067	-0.04159	0.55115	0.087

Table 8. Crystallographic Data for **2b**.

molecular formula	$C_{14}H_{18}N_2O_3$
fw, g/mol	559.5
crystal dimensions (mm)	0.57 x 0.57 x 0.57
color, shape	colorless block
crystal system	orthorhombic
space group	*P* 21 21 21
unit cell parameters	
a, Å	6.2571(3)
b, Å	12.9524(11)
c, Å	16.9737(14)
V, Å^3	1375.62(0.18)
Z	4
ρ(calc´d), g cm^{-3}	1.27
μ, cm^{-1}	0.898
diffractometer	Enraf-Nonius CAD4/Mach3
wavelength, λ, Å	0.71073
temperature, K	298
θ range	2.0 – 25.9
F(000)	560.0
reflections collected	3016 ($0 \leq h \leq 7, 0 \leq k \leq 15, -20 \leq l \leq 20$)
independent reflections	2655
reflections observed	2404 ($I > 2\sigma_I$)

R indices observed (all data)	0.032 (0.039)
wR2 observed (all data)	0.084 (0.088)
parameters (restraints)	172 (0)
Extinction coefficient	none
Goodness of fit	1.033
Shift/esd max (mean)	0.000 (0.000)
largest difference peak and hole	0.100 and –0.178 e^{-} $Å^{-3}$

Table 9. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2b**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
O(1)	1.0892(2)	0.7615(8)	0.3213(6)	0.054*
C(2)	1.0951(2)	0.7459(1)	0.4004(1)	0.043*
N(3)	1.1062(2)	0.8347(8)	0.4471(7)	0.040*
N(4)	1.1154(2)	0.9345(8)	0.4121(7)	0.042*
C(5)	0.9651(2)	0.9366(1)	0.3455(1)	0.044*
C(6)	1.0400(2)	0.8603(1)	0.2831(1)	0.047*
C(7)	0.8847(3)	0.8386(1)	0.2172(1)	0.048*
C(8)	0.6897(3)	0.7918(1)	0.2323(1)	0.055*
C(9)	0.5503(4)	0.7709(1)	0.1710(1)	0.072*
C(10)	0.6031(5)	0.7981(2)	0.0946(1)	0.083*
C(11)	0.7951(4)	0.8462(2)	0.0796(1)	0.081*
C(12)	0.9367(3)	0.8658(1)	0.1403(1)	0.065*
C(13)	0.9387(3)	1.0460(1)	0.3134(1)	0.063*
C(14)	1.3393(3)	0.9625(1)	0.3945(1)	0.056*
C(15)	1.0926(2)	0.8325(1)	0.5306(1)	0.040*
O(16)	1.0989(2)	0.7530(7)	0.5672(6)	0.052*
C(17)	1.0686(3)	0.9373(1)	0.5684(1)	0.051*
C(18)	1.0559(3)	0.9320(1)	0.6572(1)	0.062*
O(19)	1.0907(2)	0.6594(7)	0.4249(6)	0.054*

Fractional atomic coordinates and isotropic displacement parameters (Angstrom squared), with standard deviations in the least significant digits in parentheses. Anisotropically refined atoms are marked with an asterisk (*). The form of the Anisotropic displacement parameter is:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Table 10. Selected Interatomic Distances (Å) for **2b**.

Atom1	Atom2	Distance	Atom1	Atom2	Distance
O(1)	C(2)	1.359(2)	O(1)	C(6)	1.468(2)
C(2)	N(3)	1.398(2)	C(2)	O(19)	1.195(2)
N(3)	N(4)	1.423(2)	N(3)	C(15)	1.420(2)
N(4)	C(5)	1.471(2)	N(4)	C(14)	1.477(2)
C(5)	C(6)	1.522(3)	C(5)	C(13)	1.527(3)
C(6)	C(7)	1.508(3)	C(7)	C(8)	1.387(3)
C(7)	C(12)	1.391(3)	C(8)	C(9)	1.384(4)
C(9)	C(10)	1.384(3)	C(10)	C(11)	1.377(4)
C(11)	C(12)	1.382(3)	C(15)	O(16)	1.204(2)
C(15)	C(17)	1.509(2)	C(17)	C(18)	1.511(3)

Table 11. Selected Interatomic Angles (deg) for **2b**.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(2)	O(1)	C(6)	124.8(1)	O(1)	C(2)	N(3)	116.1(2)
O(1)	C(2)	O(19)	118.8(2)	N(3)	C(2)	O(19)	125.1(2)
C(2)	N(3)	N(4)	120.8(1)	C(2)	N(3)	C(15)	123.1(2)
N(4)	N(3)	C(15)	116.1(1)	N(3)	N(4)	C(5)	108.2(1)
N(3)	N(4)	C(14)	110.2(1)	C(5)	N(4)	C(14)	116.5(1)
N(4)	C(5)	C(6)	108.9(1)	N(4)	C(5)	C(13)	111.2(1)
O(1)	C(6)	C(5)	108.9(1)	O(1)	C(6)	C(7)	107.4(1)
C(6)	C(5)	C(13)	112.8(2)	C(5)	C(6)	C(7)	116.0(2)
C(6)	C(7)	C(8)	120.8(2)	C(6)	C(7)	C(12)	119.9(2)
C(8)	C(7)	C(12)	119.3(2)	C(7)	C(8)	C(9)	120.1(2)
C(8)	C(9)	C(10)	120.3(3)	C(9)	C(10)	C(11)	119.8(3)
C(10)	C(11)	C(12)	120.2(2)	C(7)	C(12)	C(11)	120.2(2)
N(3)	C(15)	O(16)	122.0(2)	N(3)	C(15)	C(17)	114.4(2)
O(16)	C(15)	C(17)	123.6(2)	C(15)	C(17)	C(18)	112.8(2)

Table 12. Torsional Angles (deg) for **2b**.

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
O(1)	C(2)	N(3)	C(15)	173.7	O(19)	C(2)	N(3)	C(15)	-6.4
C(2)	N(3)	C(15)	O(16)	10.0	C(2)	N(3)	C(15)	C(17)	-169.6
C(13)	C(5)	C(6)	C(7)	-66.4	C(5)	C(6)	C(7)	C(8)	-63.9
C(5)	C(6)	C(7)	C(12)	116.1	C(6)	C(7)	C(8)	C(9)	-179.0
C(6)	C(7)	C(12)	C(11)	-179.9	C(12)	C(7)	C(8)	C(9)	1.0
C(8)	C(7)	C(12)	C(11)	0.0	C(7)	C(8)	C(9)	C(10)	-0.9
C(8)	C(9)	C(10)	C(11)	-0.1	C(9)	C(10)	C(11)	C(12)	1.2
C(10)	C(11)	C(12)	C(7)	-1.1	N(3)	C(15)	C(17)	C(18)	-179.7
O(16)	C(15)	C(17)	C(18)	0.7					

Table 13. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **2b**.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.0664(7)	0.0449(5)	0.0516(5)	0.0159(5)	-.0031(5)	-.0044(4)
C(2)	0.0365(6)	0.0383(7)	0.0532(8)	0.0054(6)	-.0003(6)	-.0016(6)
N(3)	0.0392(5)	0.0316(5)	0.0490(6)	0.0000(5)	-.0009(5)	0.0040(4)
N(4)	0.0419(6)	0.0324(5)	0.0509(6)	-.0016(5)	-.0008(5)	0.0060(5)
C(5)	0.0439(7)	0.0399(7)	0.0480(7)	0.0026(6)	-.0016(6)	0.0039(6)
C(6)	0.0477(7)	0.0461(7)	0.0480(7)	0.0031(6)	0.0039(6)	0.0033(6)
C(7)	0.0589(8)	0.0403(7)	0.0457(7)	0.0070(7)	0.0020(7)	0.0003(6)
C(8)	0.0643(9)	0.0424(7)	0.0579(9)	-.0025(7)	-.0040(8)	0.0002(7)
C(9)	0.076(1)	0.051(1)	0.090(1)	-0.002(1)	-0.020(1)	-0.010(1)
C(10)	0.114(2)	0.064(1)	0.071(1)	0.016(1)	-0.037(1)	-0.022(1)
C(11)	0.116(2)	0.080(1)	0.046(1)	0.022(1)	0.003(1)	-0.003(1)
C(12)	0.078(1)	0.069(1)	0.050(1)	0.007(1)	0.009(1)	0.001(1)
C(13)	0.081(1)	0.044(1)	0.063(1)	0.008(1)	-0.008(1)	0.009(1)
C(14)	0.0473(8)	0.0510(9)	0.0712(10)	-.0113(6)	-.0009(7)	0.0105(8)
C(15)	0.0333(6)	0.0388(7)	0.0481(7)	-.0022(6)	-.0037(6)	0.0039(5)
O(16)	0.0602(6)	0.0415(5)	0.0539(6)	-.0009(5)	-.0041(5)	0.0082(4)
C(17)	0.0607(9)	0.0402(7)	0.0524(8)	-.0012(7)	-.0017(7)	-.0002(6)
C(18)	0.081(1)	0.050(1)	0.054(1)	-0.004(1)	-0.004(1)	-0.006(1)
O(19)	0.0608(6)	0.0344(5)	0.0678(6)	0.0039(5)	-.0008(6)	0.0005(4)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$$

Table 14. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for **2b**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq},Å^2
H(5)	0.82553	0.91336	0.36479	0.053
H(6)	1.17215	0.88716	0.25983	0.057
H(8)	0.65263	0.77424	0.28361	0.066
H(9)	0.42052	0.73858	0.18125	0.087
H(10)	0.50923	0.78390	0.05352	0.099
H(11)	0.82958	0.86567	0.02842	0.097
H(12)	1.06719	0.89726	0.12964	0.078
H(13A)	0.89044	1.09077	0.35481	0.075
H(13B)	0.83561	1.04572	0.27151	0.075
H(13C)	1.07344	1.07029	0.29370	0.075
H(14A)	1.42244	0.95917	0.44191	0.068
H(14B)	1.34425	1.03132	0.37359	0.068
H(14C)	1.39655	0.91512	0.35642	0.068
H(17A)	1.18929	0.98010	0.55356	0.061
H(17B)	0.94005	0.96999	0.54838	0.061
H(18A)	1.03917	1.00032	0.67815	0.074
H(18B)	1.18476	0.90182	0.67750	0.074
H(18C)	0.93575	0.89035	0.67228	0.074

Figure S1:

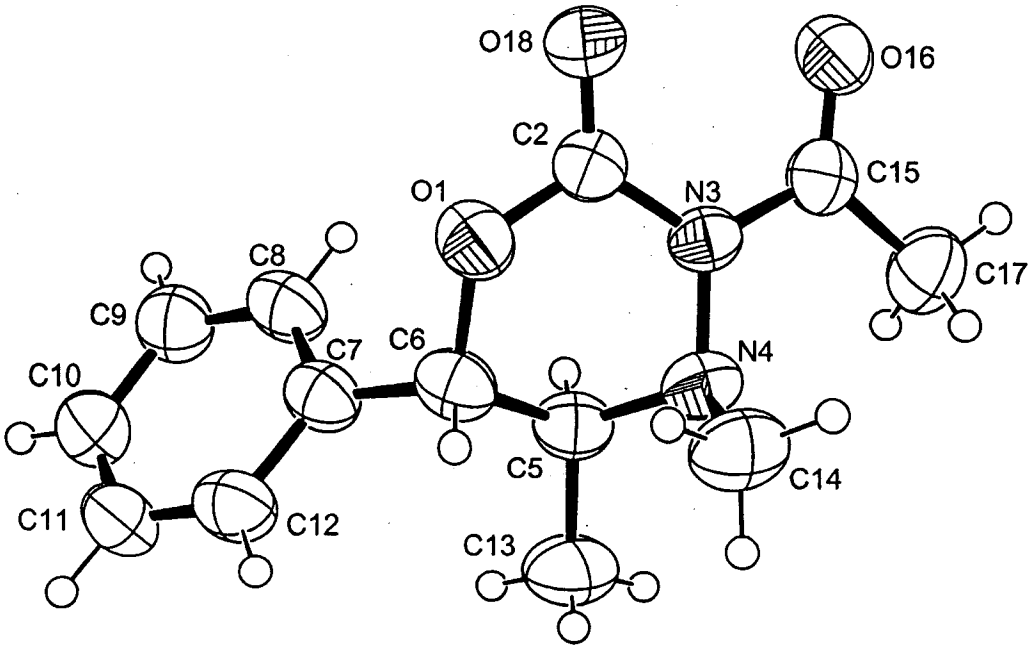
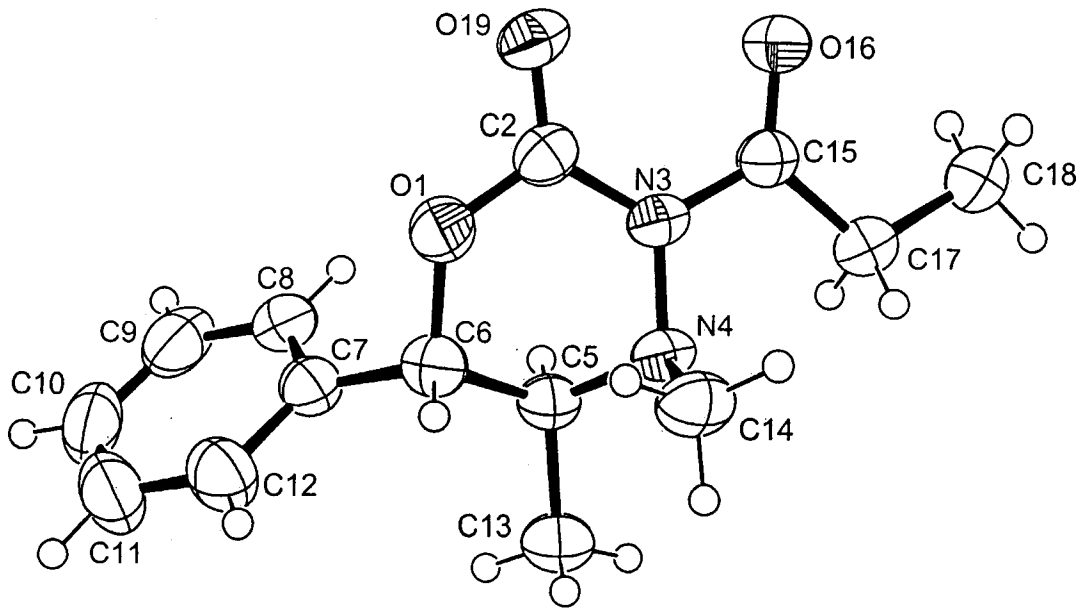


Figure S2:



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Semiempirical AM1 Calculations

In order to test the validity of semiempirical AM1 calculations, a full geometry optimization of derivative **2a** was carried out using the Gaussian98 (Rev. A.7) software package[1] and the B3LYP/6-31G* hybrid density functional method. The AM1 method[2] was selected over the PM3 method because AM1 proved superior in yielding geometries in better agreement with both the gas phase B3LYP/6-31G* calculations and the X-ray structure of derivative **2a** (Figure S3, Tables 1-3, Chart 1). Though the bond lengths in both the 6-membered ring and in the acyl group were slightly larger in the AM1, PM3, and B3LYP structures than those of the X-ray structure, the AM1 results were in general much closer to both the B3LYP and X-ray results than the PM3 results. In addition, the PM3 results predict the carbonyl groups in **2a** to be much more skewed than either the AM1 or the B3LYP results. Therefore, the AM1 method was adopted for extensive gas phase studies of both local minima and transition states for a variety of derivatives. All local minima and transition states were verified by vibrational frequency calculations, and in all cases, transition states reported exhibited a single imaginary vibrational frequency.

Figure S3. Comparison of Calculated and X-ray Structures

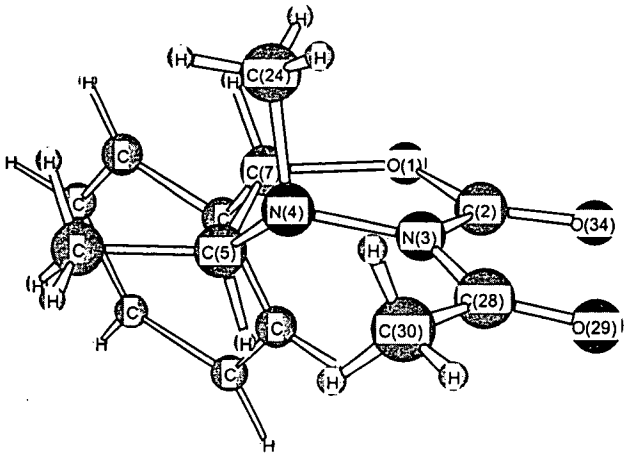


Table 1. Comparison of Bond Lengths in Calculated and X-ray crystal structures.

Bond Length (Å)	AM1	PM3	DFT	X-ray
O1-C2	1.383	1.358	1.361	1.344
C2-N3	1.421	1.446	1.415	1.391
N3-N4	1.389	1.475	1.418	1.415
N4-C5	1.492	1.500	1.473	1.465
C5-C7	1.551	1.549	1.543	1.509
C7-O1	1.437	1.435	1.457	1.455
C2-O34	1.230	1.213	1.203	1.188
N3-C28	1.431	1.500	1.423	1.396
C28-O29	1.235	1.208	1.212	1.200

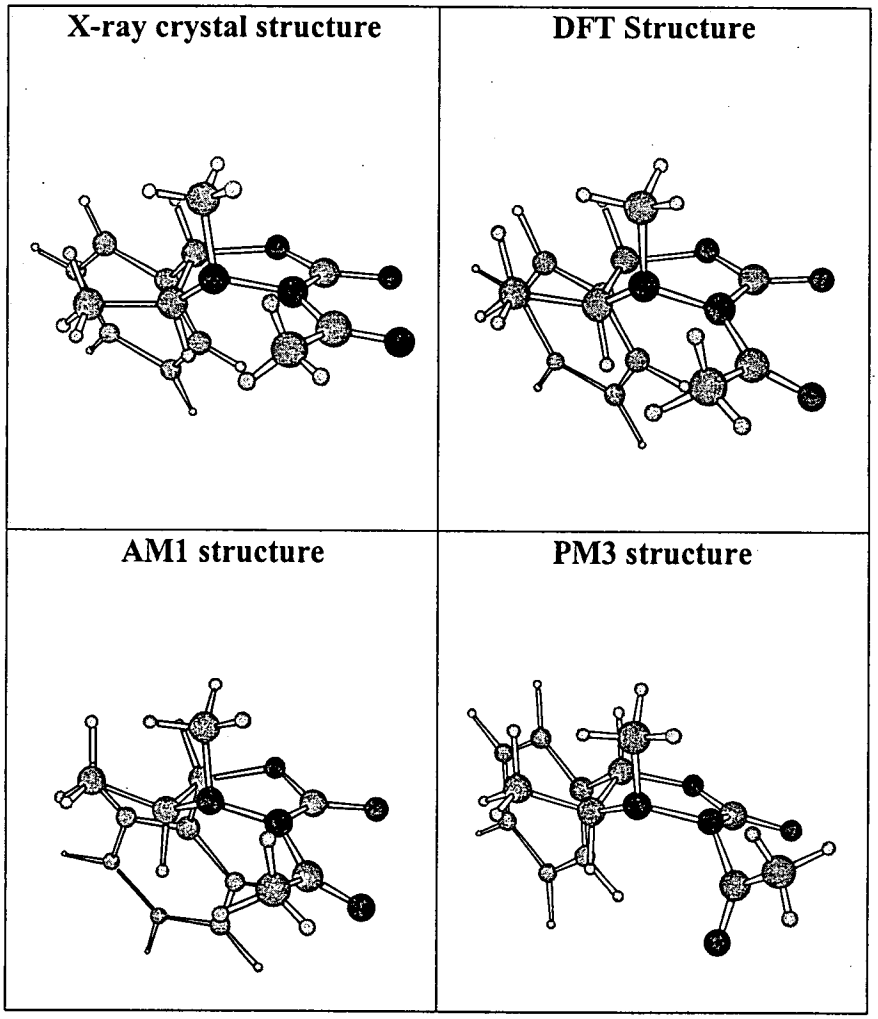
Table 2. Comparison of Bond Angles in Calculated and X-ray crystal structures.

Bond Angle (degrees)	AM1	PM3	DFT	X-ray
O1-C2-N3	118.8	123.6	115.0	116.7
C2-N3-N4	119.7	118.0	118.8	120.0
N3-N4-C5	110.3	111.6	107.8	108.0
N4-C5-C7	114.0	111.7	109.9	109.5
C2-N3-C28	120.4	116.6	122.9	123.0
N4-N3-C28	119.0	111.0	118.0	116.8
N3-C28-O29	118.9	118.7	122.0	121.9
N3-C28-C30	118.2	114.6	115.2	116.0

Table 3. Comparison of Dihedral Angles in Calculated and X-ray crystal structures.

Dihedral Angle (degrees)	AM1	PM3	DFT	X-ray
O34-C2-N3-C28	-23.4	-40.5	-26.5	-8.5
C2-N3-C28-O29	-6.0	-60.0	-3.9	4.5

Chart 1. Comparison of Calculated and X-ray Crystal Structure



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