JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
J. Am. Chem. Soc., 1997, 119(37), 8699-8711, DOI:10.1021/ja970990x

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at http://pubs.acs.org/page/copyright/permissions.html

ACS Publications
MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1997 American Chemical Society

Table 1S. Comparison of Structures for **6** - **12** Optimized at MP2 and DFT Levels.

Compound	Bond length/ angle	MP2/6-311G*	BPW91/6-311G*
1,3-diaminobenzene[a]	C1-C2	1.401	1.407
	C3-C4	1.404	1.411
	C5-C6	1.396	1.396
	C2-H	1.090	1.095
	C4-H	1.088	1.093
	C5-H	1.088	1.093
	C1-N7	1.405	1.402
	N7-H	1.010	1.016(1.019)
	C1-C2-C3	121.3(121.6)	121.2
	C2-C3-C4	119.2	119.1
	C3-C4-C5	119.6	119.5
	C4-C5-C6	121.2	121.6
	C1-C2-H	119.4	119.4
	C3-C4-H	120.0	120.0
	C4-C5-H	119.4	119.2
	Ha-N-Hb	110.4	111.1(111.3)
	ρ_e	47.0 (46.8)	42.8(42.3)
	ϵ	3.4 (4.3)	2.8
	V_i, cm^{-1}	1827.3 (1774.2)	762.8 (741.4)

Table 1S, cont'd

1,3,5-triaminobenzene[b]			
	C1-C2	1.400	1.406
	C2-H2	1.089	1.093
	C1-N1	1.406	1.403
	N1-Ha	1.010	1.016
	N1-Hb	1.010	1.016
	C1-C2-C3	120.2	120.1
	C2-C3-C4	119.8	119.9
	C1-C2-H2	119.9	120.0
	C2-C1-N1	120.0	120.0
	Ha-N1-Hb	110.4 (110.8)	111.2 (110.9)
	Ha-N5-Hb	110.4 (109.9)	111.2 (110.9)
	ρ_e(N1,N3)	47.0 (46.9)	43.2 (43.8)
	ρ_e(N5)	47.0 (47.5)	43.2 (43.8)
	ϵ(N1,N1)	4.1 (0.5)	2.6 (2.6)
	ϵ(N5)	4.1 (0.5)	2.6 (2.6)
	V_i, cm^{-1}	2780.8 (2727.7)	1355.7 (1282.6)
2-aminopyrimidine	N1-C2	1.347	1.356
	N3-C4	1.337	1.338
	C4-C5	1.394	1.399
	C2-N3	1.373	1.367
	C4-H4	1.089	1.096
	C5-H5	1.084	1.090
	N3-H	1.007	1.012

Table 1S, cont'd

	N1-C2-N3	127.0	127.0
	C2-N3-C4	115.6	115.3
	N3-C4-C5	122.8	123.3
	C4-C5-C6	116.2	115.8
	N1-C2-N7	116.5	116.5
	N3-C4-H4	115.8	115.6
	C4-C5-H5	121.9	122.1
	H-N7-H	116.4	119.0
	ρ_e	37.1	23.7
	ϵ	2.3	1.2
	V_i, cm^{-1}	324.6	22.7
	V_r, cm^{-1}	4598. @ 59.6°	5558. @ 60.9°
4-aminopyrimidine	N1-C2	1.336	1.341
	C2-N3	1.340	1.340
	N3-C4	1.342	1.352
	C4-C5	1.407	1.415
	C5-C6	1.386	1.387
	C6-N1	1.347	1.351
	C2-N3	1.376	1.369
	C2-H2	1.088	1.095
	C5-H5	1.086	1.092
	N7-Ha	1.009	1.014
	N7-Hb	1.007	1.012
	N1-C2-N3	128.0	128.4

Table 1S, cont'd

C2-N3-C4	116.3	116.1
N3-C4-C5	121.1	121.0
C4-C5-C6	116.8	116.6
C5-C6-N1	123.2	123.6
C6-N1-C2	114.6	114.3
N3-C4-N7	116.5	116.0
N1-C2-H2	116.4	116.2
C4-C5-H5	121.8	122.0
N1-C6-H6	116.2	116.0
Ha-N7-Hb	114.9	117.1
φ_e	84.1	83.8
ρ_e	38.1	26.0
ϵ	2.8	1.8
V_i, cm^{-1}	312.5	66.3
V_r, cm^{-1}	2950. @ 59.8°	4010. @ 60.9°

4,6-diaminopyrimidine[a]

N1-C2	1.335	1.337
N3-C4	1.347	1.357
C4-C5	1.397	1.404
C4-N7	1.380	1.376
C2-H2	1.088	1.096
C5-H5	1.087	1.093
N7-Ha	1.009	1.015
N7-Hb	1.007	1.013

Table 1S, cont'd

	N1-C2-N3	128.4	128.8
	C2-N3-C4	115.3	115.2
	N3-C4-C5	122.1	122.1
	C4-C5-C6	116.8	116.7
	N1-C2-N7	115.8(116.1)	115.5
	N1-C2-H2	115.8	115.6
	C4-C5-H5	121.6	121.6
	Ha-N7-Hb	114.4(114.5)	115.9(116.0)
	φ_e	83.9(84.1)	83.8(83.6)
	ρ_e	40.2(39.7)	32.5(32.1)
	ϵ_e	3.0(3.2)	2.5
	V_i, cm^{-1}	795.8 (754.8)	194.9 (173.3)
2,4,6-triaminopyrimidine[c]			
	N1-C2	1.340	1.347
	N3-C4	1.342	1.349
	C4-C5	1.398	1.405
	C2-N7	1.376	1.377
	C4-N8	1.381	1.382
	C5-H5	1.085	1.091
	N7-Ha,Hb	1.007	1.013
	N8-Ha	1.009	1.015
	N8-Ha	1.007	1.014
	N1-C2-N3	127.8	127.9
	C2-N3-C4	115.4	115.3

Table 1S, cont'd

	N3-C4-C5	122.7	122.7
	C4-C5-C6	116.1	116.1
	N1-C2-N7	116.0	116.1
	N3-C4-N8	115.6	115.5
	C4-C5-H5	121.9	122.0
	Ha-N7-Hb	116.1 (115.9,116.2)	117.1 (117.0, 117.3)
	Ha-N8-Hb	114.2 (114.3,114.4)	115.2 (115.2, 115.3)
	Ha-N9-Hb	114.2 (114.3,114.4)	115.3 (115.2, 115.3)
	ρ_e(N7)	38.9 (39.8, 38.5)	33.3 (33.9, 33.4)
	ρ_e(N8)	41.0 (40.8, 40.4)	35.9 (35.6, 35.1)
	ρ_e(N9)	41.0 (40.8, 40.4)	36.4 (35.6, 35.1)
	φ_e(N8)	-84.9 (85.1, 84.1)	-83.9 (84.9, 84.0)
	φ_e(N9)	-84.7 (-85.1, -84.1)	-84.9 (-84.9, -84.0)
	ϵ_e(N7)	2.4 (2.9, 1.8)	1.6 (2.2, 1.0)
	ϵ_e(N8)	2.8 (3.0, 2.9)	2.1 (2.3, 2.1)
	ϵ_e(N9)	3.0 (3.0, 2.9)	2.3 (2.3, 2.1)
	V_i, cm^{-1}	1231.1 (1229.4, 1157.2)	442.2 (436.0,400.0)
Desoxyminoxidil[d]	N1-C2	1.339	1.346
	C2-N3	1.342	1.351
	N3-C4	1.344	1.351
	C4-C5	1.395	1.408
	C5-C6	1.403	1.414
	C6-N1	1.351	1.358
	C2-N7	1.381	1.383

Table 1S, cont'd

C4-N8	1.385	1.387
C6-N9	1.385	1.387
C5-H5	1.082	1.089
N7-Ha,Hb	1.012	1.016
N8-Ha	1.014	1.019
N8-Ha	1.013	1.017
N1-C2-N3	127.9	128.2
C2-N3-C4	114.6	114.3
N3-C4-C5	123.4	123.5
C4-C5-C6	116.6	116.6
C5-C6-N1	121.2	121.0
C6-N1-C2	116.3	116.4
N1-C2-N7	116.0	116.0
N3-C4-N8	115.3	115.3
N1-C6-N9	115.9	115.9
C4-C5-H5	120.0	119.9
Ha-N7-Hb	115.1 (115.3,115.3,115.5)	116.2 (116.4)
Ha-N8-Hb	113.5 (113.3,113.5,113.7)	114.3 (114.5)
Ca-N9-Cb	111.2	114.6
φ_e(N8)	84.9 (-84.8,-83.8,83.9)	-84.4 (84.7)
φ_e(N9)	-88.1 (-87.7,-89.2,-86.6)	-91.6 (-91.1)
ρ_e(N7)	41.0 (40.2, 40.2, 39.5)	36.7 (36.0)
ρ_e(N8)	41.8 (42.4, 41.7, 41.2)	38.6 (37.9)
ρ_e(N9)	32.2 (32.1, 32.5, 31.9)	15.2 (14.7)
ϵ_e(N7)	3.3 (2.5, 2.5, 1.7)	2.2 (1.5)

Table 1S, cont'd

ϵ_e(N8)	3.0 (3.2, 3.1, 2.8)	2.6 (1.7)
ϵ_e(N9)	3.1 (2.9, 3.0, 3.0)	1.8
V_i, cm^{-1}	743.2 (742.3,738.4,652.9)	434.8 (402.2)

[a] Values in parentheses are for the syn isomer, only if different by more than 0.001 Å or 0.1°)

[b] Values in parentheses are for the syn-syn [$1^+3^+5^+$] isomer, only if different by more than 0.001 Å or 0.1°)

[c] Values are for the $2^+4^-6^+$ isomer. Values are given in parentheses for the $2^-4^+6^+$ and $2^+4^+6^+$ isomers, but only if they differ by more than 0.001 Å in bond lengths or 0.1° in angles.

[d] The MP2 results are for the lowest energy $2^+4^-6^-$ isomer. Values are given in parentheses for the $2^-4^+6^-$, $2^+4^+6^-$), and $2^+4^+6^+$) isomers if they differ by more than 0.001 Å in bond lengths or 0.1° in angles. The BPW91 results correspond to the lowest energy $2^-4^+6^-$ isomer. Values in parentheses are give for the $2^+4^+6^+$ isomer.

Table 2S. GIAO Calculated Averages of Chemical Shifts over Torsional/Rotational Motions for Aniline, 2-Aminopyrimidine, and 4-Aminopyrimidine

Compound	Atoms	H*M*	B**M*	B**B*
Aniline	C1	0.0	1.2	-0.6
	C2,C6	1.2	1.8	-0.4
	C3,C5	-0.2	0.0	0.0
	C4	0.6	1.0	-0.4
	N7	1.4	-0.5	-2.4
2-Aminopyrimidine	C2	-0.9	0.8	-0.1
	C4, C6	0.2	0.0	0.0
	C5	-0.7	0.3	0.0
	N1, N3	-2.5	1.3	-0.2
	N7	-0.4	0.6	0.0
4-Aminopyrimidine	C2	0.1	0.1	0.0
	C4	-1.0	0.9	-0.2
	C5	-1.0	0.6	-0.3
	C6	0.0	0.1	0.0
	N1	-2.0	1.0	-0.6
	N3	-2.0	1.8	-0.3
	N7	-0.9	-0.2	-0.6

Figure Captions

Figure 1S. For the carbons of aniline **3** these are surface and contour plots of the calculated ($B^{**}B^{*}$) ^{13}C chemical shifts $\delta(Ci,\varphi,\rho)$ versus the angles φ and ρ. a) the C1 (*ipso*-) carbon: the contour lines are separated by 1 ppm; b) the C2 (*ortho*-) carbon: the contour lines are separated by 2 ppm; c) the C3 (*meta*-) carbons: the contour lines are separated by 0.2 ppm; and d) the C4 (*para*-) carbon: the contour lines are separated by 2 ppm.

Figure 2S. Calculated (BPW91/STO-3G//BPW91/6-311G*) surface and contour plots for the $2p_z$ Mulliken populations $q_z(Ci,\varphi,\rho)$ at each of the carbons in aniline **3** plotted as a function of the angles φ and ρ: a) the C1 (*ipso*-) carbon: the contour lines are separated by 0.010; b) the C2 (*ortho*-) carbon: the contour lines are separated by 0.010; c) the C3 (*meta*-) carbon: the contour lines are separated by 0.005 and d) the C4 (*para*-) carbon: the contour lines are separated by 0.005.

Figure 3S. For the carbons and ring nitrogens of 4-aminopyrimidine **9** these are the surface and contour plots for calculated ($B^{**}B^{*}$) ^{13}C and ^{15}N chemical shifts $\delta(Ci,\varphi,\rho)$ and $\delta(Ni,\varphi,\rho)$ as functions of the angles φ and ρ. a) the C4 (*ipso*-) carbon: the contour lines are separated by 2 ppm; b) the N3 (*ortho*-) nitrogen: the contour lines are separated by 5 ppm; c) the C5 (*ortho*-) carbon: the contour lines are separated by 2 ppm; d) the C2 (*meta*-) carbon: the contour lines are separated by 0.05 ppm; e) the C6 (*meta*-) carbon: the contour lines are separated by 0.05 ppm; f) the N1 (*para*-) nitrogen: the contour lines are separated by 2.5 ppm.

Figure 4S. Calculated (BPW91/STO-3G//BPW91/6-311G*) surface and contour plots for the $2p_z$ Mulliken populations $q_z(C4,\varphi,\rho)$ and $q_z(N3,\varphi,\rho)$ at the carbons and ring nitrogens of 2-aminopyrimidine **8** plotted as a function of the angles φ and ρ: a) the C4 (*ipso*-) carbon: the contour lines are separated by 0.005; b) the N3 (*ortho*-) nitrogen: the contour lines are separated by 0.010; c) the C5 (*ortho*-) carbon: the contour lines are separated by 0.010; d) the C2 (*meta*-) carbon: the contour lines are separated by 0.002; e) the C6 (*meta*-) carbon: the contour lines are separated by 0.002; f) the N1 (*para*-) nitrogen: the contour lines are separated by 0.005.

Figure 1S

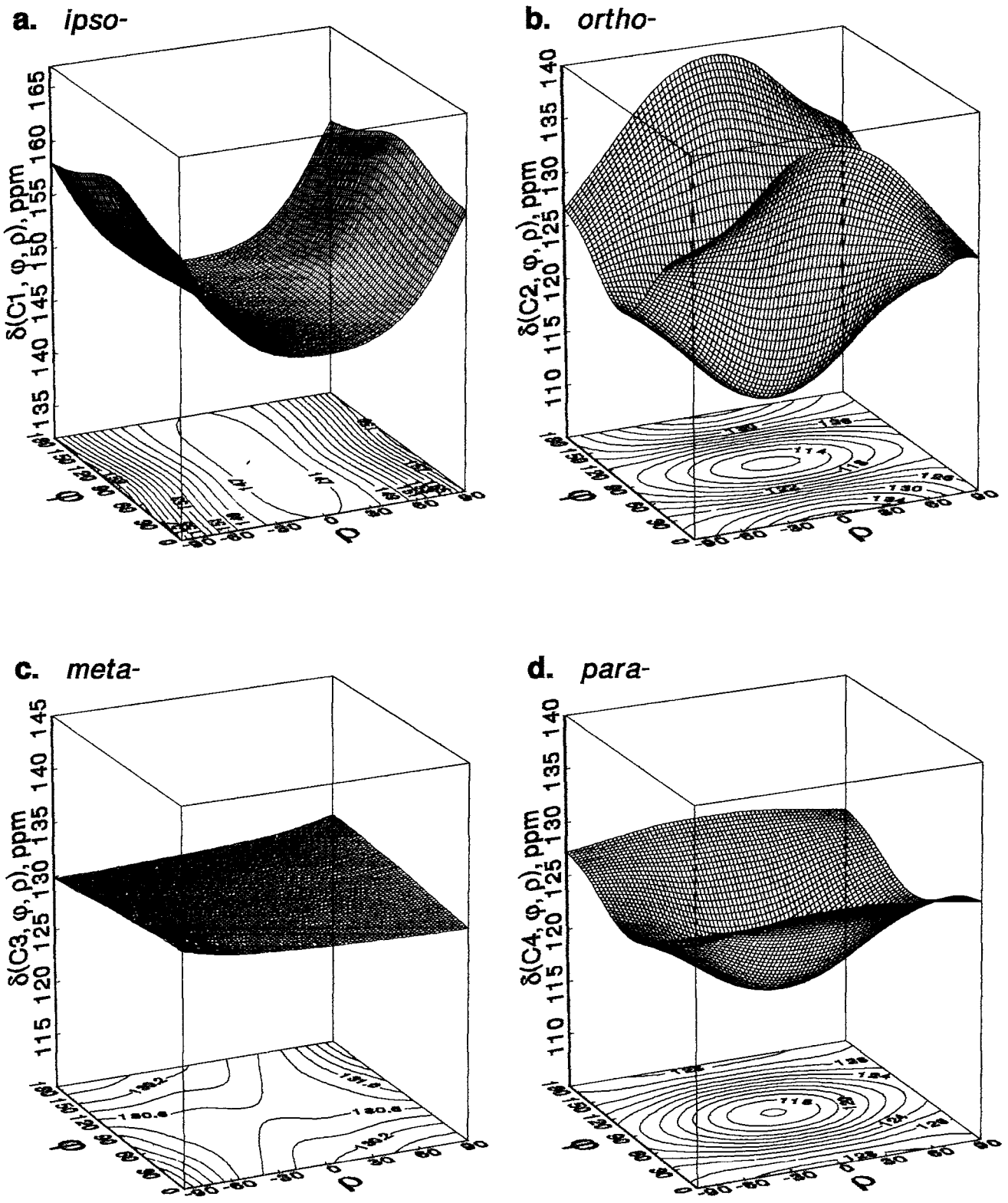

a. ipso-
δ(C1, φ, ρ), ppm
b. ortho-
δ(C2, φ, ρ), ppm
c. meta-
δ(C3, φ, ρ), ppm
d. para-
δ(C4, φ, ρ), ppm
φ
ρ

Figure 2S

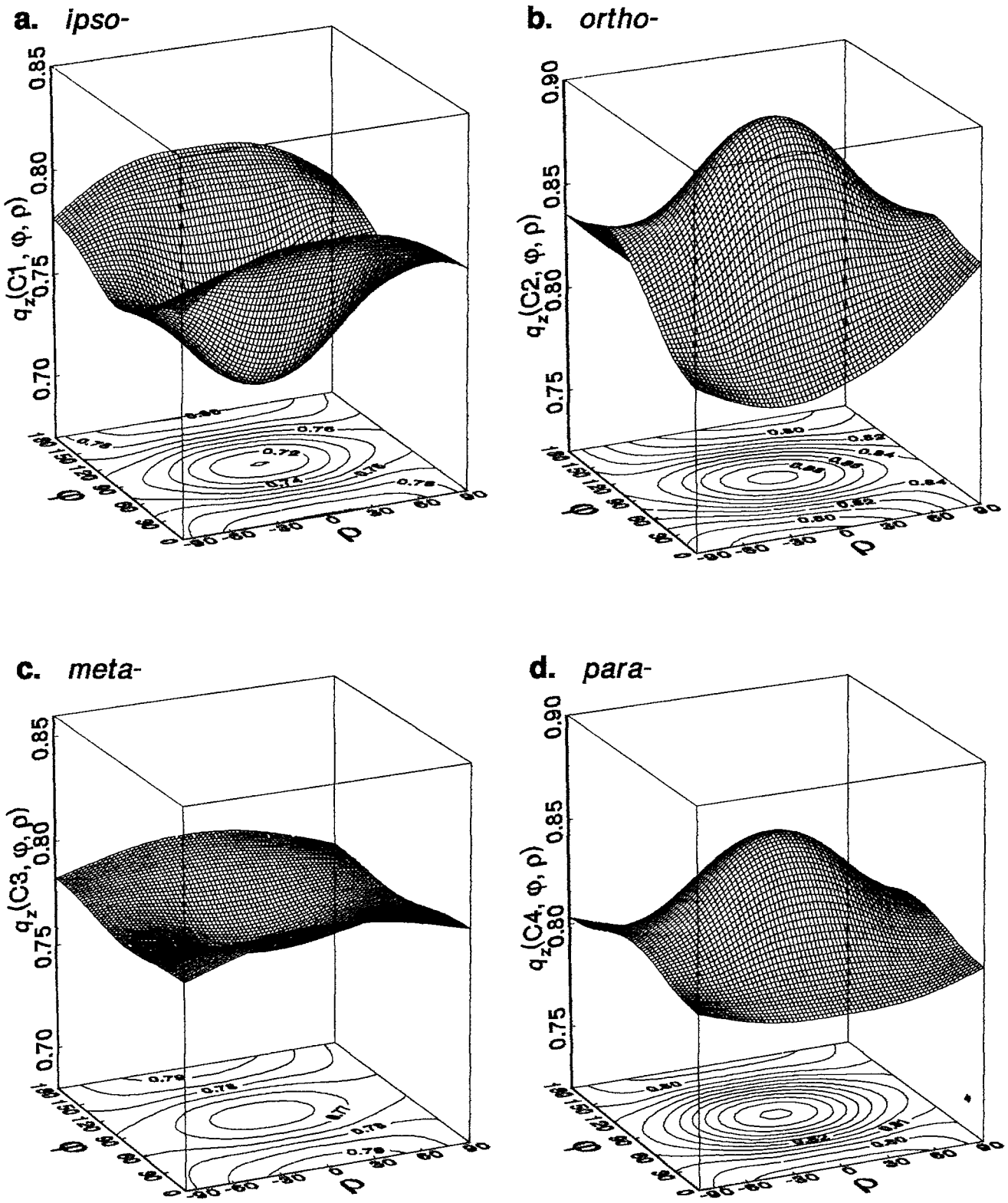

a. ipso-
b. ortho-
c. meta-
d. para-
$q_z(C1, \varphi, \rho)$
$q_z(C2, \varphi, \rho)$
$q_z(C3, \varphi, \rho)$
$q_z(C4, \varphi, \rho)$
φ
ρ

Figure 3S

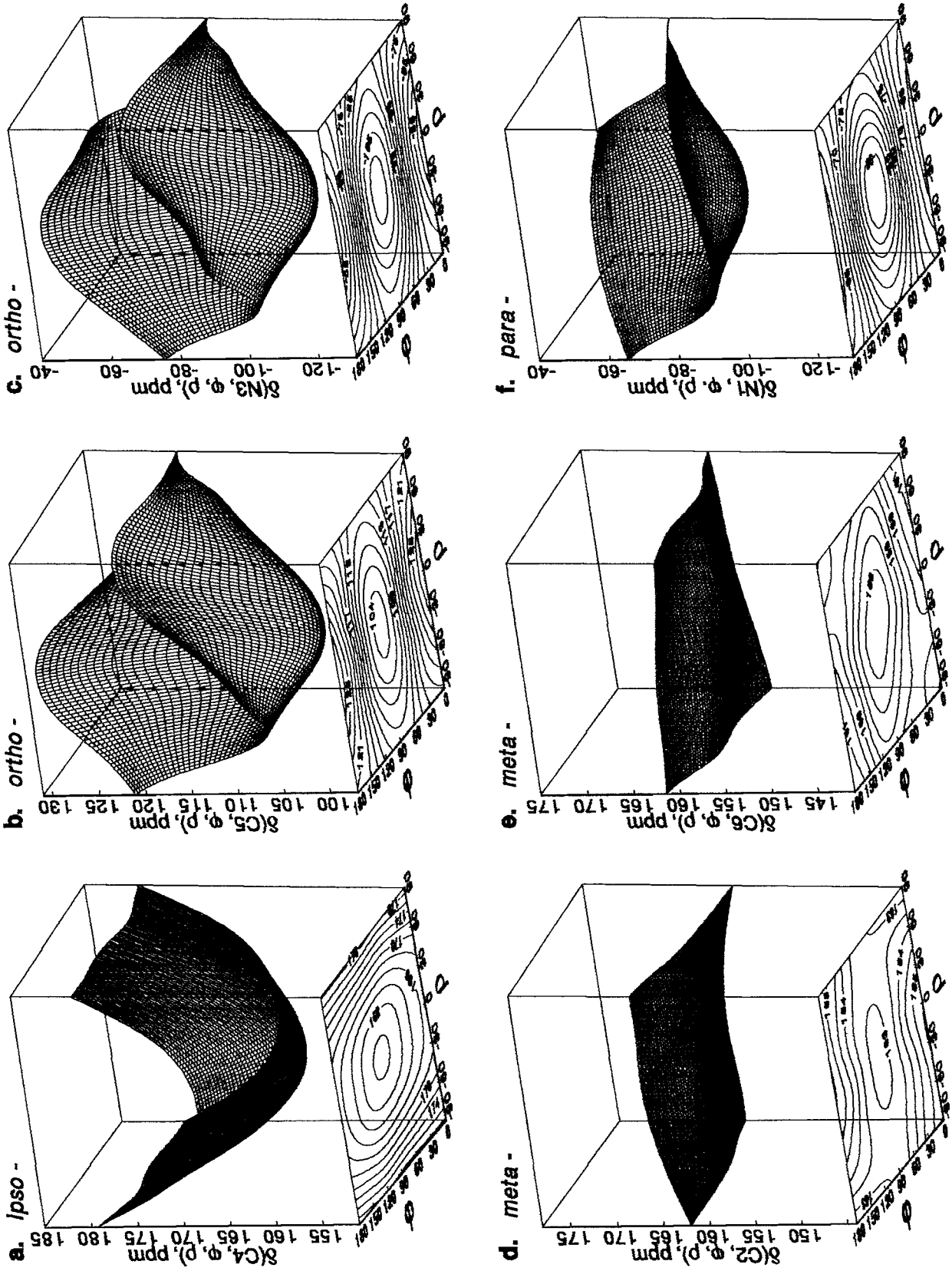
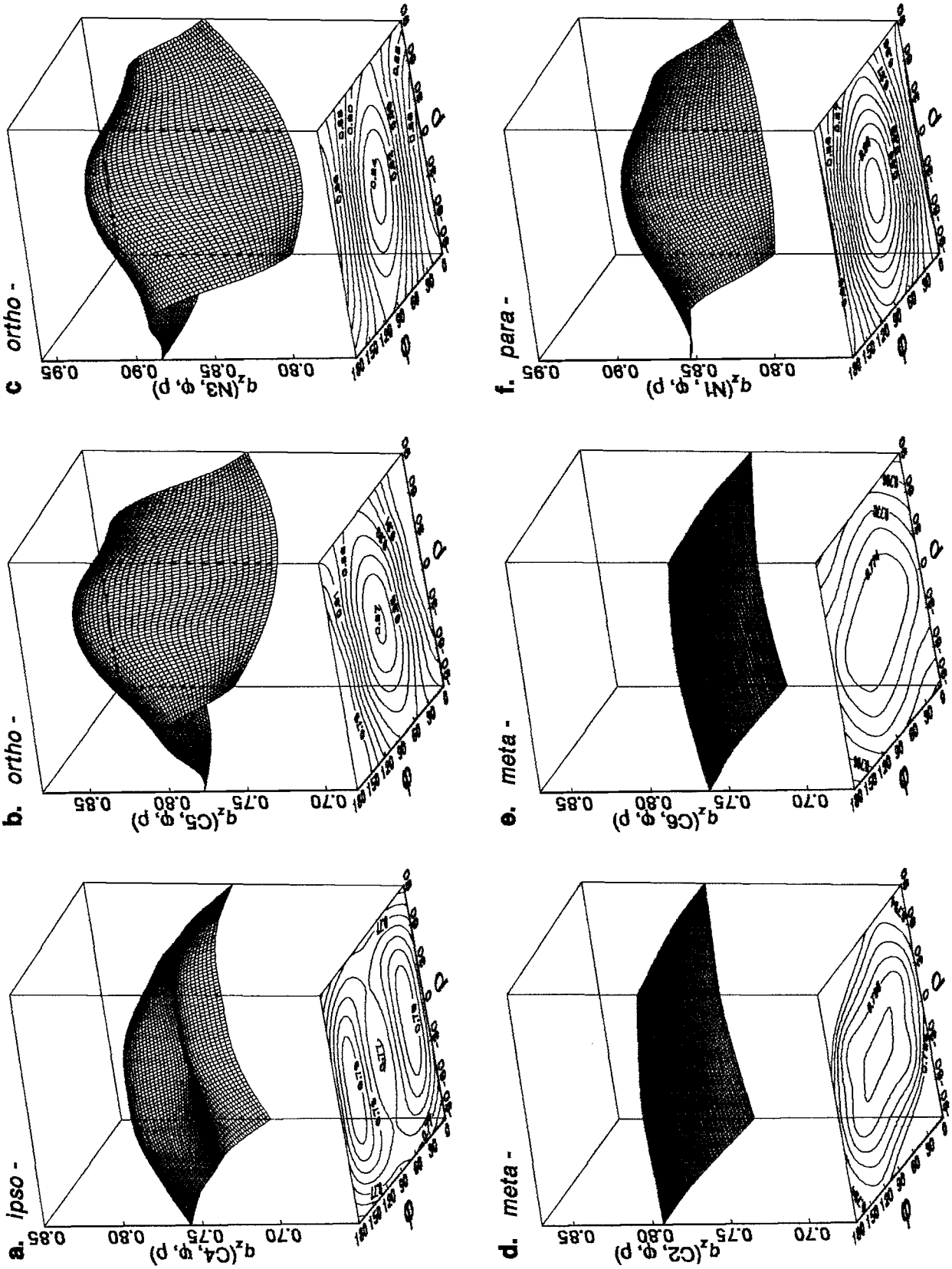

a. Ipso -
δ(C4, φ, ρ), ppm
155 160 165 170 175 180 185
b. ortho -
δ(C5, φ, ρ), ppm
100 105 110 115 120 125 130
c. ortho -
δ(N3, φ, ρ), ppm
-40 -60 -80 -100 -120
d. meta -
δ(C2, φ, ρ), ppm
150 155 160 165 170 175
e. meta -
δ(C6, φ, ρ), ppm
145 150 155 160 165 170 175
f. para -
δ(N1, φ, ρ), ppm
-40 -60 -80 -100 -120
φ
ρ

Figure 4s


a. ipso -
b. ortho -
c ortho -
d. meta -
e. meta -
f. para -
q_z(C4, φ, p)
q_z(C5, φ, p)
q_z(N3, φ, p)
q_z(C2, φ, p)
q_z(C6, φ, p)
q_z(N1, φ, p)
0.70
0.75
0.80
0.85
0.90
0.95
φ
α